MECHANOCHEMISTRY AND THE COLLOID MILL

Including the

PRACTICAL APPLICATIONS OF FINE DISPERSION

BY

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Preface

For several years so-called colloidal chemistry has been taking rapid strides, and far-seeing scientists have predicted it to be the chemistry of tomorrow, while, as a matter of fact, it is actually the chemistry of today. Developments in this interesting branch of science started in 1861, at which time Thomas Graham, who was Professor of Chemistry at University College, London, demonstrated that many ordinary substances such as sugar, salt, etc., when dissolved in water, yielded a solution quite homogeneous; such substances could be caused to crystallize and were termed crystalloids. The second type of solution Graham discovered contained such materials in aggregates which were large compared with the molecular dimensions of the crystalloid, and these he termed colloids, from the Greek meaning glue-like in appearance. The properties of such so-called solutions were very different from those of the crystalloidal. This division was maintained as long as the so-called colloidal substances were looked upon strictly from a chemical viewpoint, and it is only since the rapid advances in physical chemistry over the past twenty-odd years that we have learned to view colloids as a state of matter rather than a different type of chemistry.

This new science of mechanical dispersion, involving the principles of physical chemistry, I am calling "Mechanochemistry," because it involves dispersion or deflocculation by mechanical means rather than by chemical. While theoretical points are brought up frequently, this is done entirely with the desire of assisting in visualizing the problem and working with some degree of intelligence in trying to solve some of the mysteries of the so-called colloidal state of matter. One may proceed on such investigation by a sort of trial and error method, but this, as a rule, does not lead to satisfactory results, as in such instances it is largely a matter of good fortune. It is with the hope of eliminating the guess method in such operations that this book on the elementary theories of fine dispersion, or what we might call mechanical chemistry, was written. An attempt has been made to direct all industrial work with the idea of keeping well in mind the elementary principles of physical chemistry, and it is hoped that the subject matter has been presented in a form easy to comprehend by those interested in mechanical dispersions.

From the rapid developments made within the past few years in fine dispersion, by use of the so-called colloid mill, there seems very

little doubt but that within a few years' time the colloid mill will be a necessary piece of equipment for a great number of industries, and it is hoped that those who work with such machines in the future will acquire sufficient theoretical knowledge to conduct their investigation along the correct lines. Some of the larger corporations have realized this and such a method of procedure is now being carried on in their research departments.

the writing of this book it has been necessary to give frequent references to other works pertaining to various phases of colloidal chemistry, and an attempt has been made to connect the various problems in fine dispersion and to show the intimate relation that exists throughout, whether the problem is a dispersion in gas, liquid or solid. In referring to the work of others, I have tried in every instance to give full credit for such work to the original author on the subject, but in some instances this was very difficult to obtain, so that credit in that case has been given to the source from which the information was abstracted.

I should appreciate having called to my attention any errors or omissions that may occur in the first edition of this book, so that they may be corrected in future editions; I should also appreciate suggestions relating to change in subject matter, for which due acknowledgment and credit will be given.

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Chapter I.

Introduction.

In studying the subject of mechanical dispersion, deflocculation and disintegration, as well as the practical applications of the making of emulsions and other colloidal dispersions, it is necessary to acquire a good fundamental knowledge of the colloid state of matter It is therefore important to briefly review the past work and thus benefit by the experience of others who in the early stages of the development of this science have applied the principles of so-called colloid chemistry, since the greatest progress has been made in this manner. Without some knowledge of this subject little progress will be made, for the mechanical side of the subject only amounts to about twenty per cent of the total requirements, and it is necessary that the manufacturer or chemist in charge of the work be in possession of a knowledge of the physical-chemical principles applied, in order to operate successfully on a commercial basis. Many theories have been advanced from time to time to explain some of the results accomplished, and it is better to commence with a historical sketch and advance to the present-day applications, for without this background one will have difficulty in grasping and sensing the situation, which is a great advantage in making rapid progress

This new science of mechanical dispersion involving the use of principles in physical chemistry we shall call *Mechanochemistry* for lack of a better name, as it involves dispersion or deflocculation by mechanical means, thereby bringing about so-called colloidal dispersions.

There are few phases of solution which have attracted so much attention as colloids, and we are frequently reminded of the remarkable properties possessed by matter in the so-called colloidal state. The colloidal state of matter has been known for over half a century but

this subject has come to the front in recent years, as our understanding of it has advanced. The Italian chemist, Selmi, as early as 1844 recognized the difference between true solutions and apparent solutions of such substances as sulfur, Berlin blue and the like, and designated these as pseudo-solutions, that is, false solutions. He recognized that there were certain fundamental differences between true solutions and those which he designated as pseudo-solutions and he pointed out that when the latter were formed no change in temperature was produced He therefore assumed that in these pseudo-solutions the substance was in the state of an emulsion or suspension.

The first to study colloids extensively was the English chemist, Thomas Graham.[1] He found that compounds which readily form crystals diffuse rapidly through membranes made of vegetable parchment and other organic materials, while non-crystalline or amorphous substances either do not diffuse at all or do so very slowly when in a state of so-called solution. Graham called the solutions which readily diffused through these membranes crystalloids, and those which did not diffuse were designated colloids. Common salt (sodium chloride) is an illustration of a typical crystalloid, while gelatin is a typical colloid, according to the original ideas of Graham, for if a solution of common salt is placed on one side of a membrane of vegetable parchment, with water on the other side, in a very short time the salt will diffuse through the membrane into the clear water, and, of course, can be readily·detected. The salt solution will distribute itself equally on both sides of the membrane. If, however, a solution of gelatin is placed on one side of this membrane, it will not pass through, or diffuse, even though the solution may be very dilute. Graham termed his apparatus for diffusion and differentiation between colloids and crystalloids a *dialyser*.[2]

FIG. 1—Type of Dialyser Used by Graham.
Courtesy of Eimer & Amend.

Von Weimarn[3]. studied the precipitates formed by bringing together solutions of certain concentrations He found that they were crystalline and that when the solutions were progressively diluted, the crystals were smaller and smaller and finally could only be seen by the use of the ultra-microscope. He came to the conclusion that when very dilute solutions are brought together and form a colloidal particle, these particles are also crystalline. It is admitted by most people who are studying the colloidal state today that it is merely a state of matter,

[1] Graham, *Phil Trans*, 151, 183 (1861).
[2] Graham, *J. Chem.*, 15, 216 (1862).
[3] Von Weimarn, *Kolloid-Z.*, 2, 76 (1907).

ınd the conditions under which the product is formed determine
ᴡhether it is to be classified as a crystalloid or as a colloid.

From the very start of the investigation of the colloidal state of
natter there has been a great tendency to regard reactions occurring
)etween colloids and foreign substances as governed by chemical laws,
ᴉence arose the expression "Colloid Chemistry" which is still used
Ⅴow that physics is encroaching upon chemistry and the important
ᴉew science of physical chemistry has taken rapid strides, we are
naking more progress in the advance of the study of the colloidal state
)f matter. As an illustration, a great amount of time has been con-
ᴜmed in investigations, the object of which was to determine the
)hysical constants and the chemical compositions of colloids. These
ᴉnvestigations are now all obsolete because they did not give any con-
ordant results,[4] and although modern colloid chemistry began with
Ⅰraham, his distinction between crystalloids and colloïds has been more
ʳ less dropped, for a colloidal substance is not necessarily amorphous.
ᶠor example, colloidal gold is crystalline, while colloidal ferric oxide
ᴉay be amorphous Hence, a material is now said to be in the col·
)idal state instead of its being called a colloidal substance and we call
ᴉny phase colloidal when sufficiently divided or dispersed without defi-
ᴉitely committing ourselves to the degree of subdivision.

The prevailing theory of colloids today is that they are suspensionᵣ
f finely divided particles in a liquid. This theory is in accord with
he microscopic and ultra-microscopic investigations of colloids, for
he coarser suspensions can be seen with the microscope and some of
he finer with the ultra-microscope, while in some cases the particles
ʳe so finely dispersed that they are even beyond the limit of the ultra-
ᴉicroscope. Numerous experiments have been conducted to corrobo-
ate the theory. The particles have been filtered out under pressure
ᴉrough porous porcelain. Some were filtered out completely by thiᵣ
ᴉeans, while others were of sufficiently fine grain to pass through In
ᴇrms of this theory, the colloidal particles are simply in a state of
ᴉechanical suspension in the liquid, the properties of the colloid being
rincipally a function of the size of the particles. The whole theory
f colloidal solutions is based on the assumption that we are dealing
ᴡith two-phase systems. There is no difficulty in demonstrating the
xistence of a second phase.

ᶜOLLOID NOMENCLATURE

In the early work of Graham certain terms were used which have
een followed in modern work and are commonly applied today in

[4] Kopaczewski, in Alexander's "Colloid Chemistry," Vol. 1, Chemical Catalog
ᴏ, New York, 1926, p 547, *also see* Bancroft, "Applied Colloid Chemistry," 2nd
ᴉ, McGraw-Hill Book Co, New York, 1926, p 1.

defining colloids. Among these are the following: When both of the constituents were liquid he termed the system a sol. If one of the constituents was solid, thus making it appear to be jelly-like, he termed it a *gel*. Graham also discovered that other liquids than water are capable of forming so-called colloidal solutions; for example, alcohol and glycerol. Therefore, he differentiated as follows:—colloidal solutions in water were termed *hydrosols* and *hydrogels;* those in alcohol, *alcosols* and *alcogels;* while those in glycerol were termed *glycerosols* and *gylcerogels*. These terms, as originally brought out by Graham, are still used in colloid chemistry nomenclature.

As our knowledge in colloid science developed, it was found necessary to supplement Graham's nomenclature with other terms. According to the modern conceptions true solutions, colloidal solutions and colloidal suspensions are related terms, differing merely in the state of division of the dissolved substances. A true solution, if not further dissociated, usually is in a molecular condition. An example is the case of sugar dissolved in water. In a true solution we have an equal distribution of a substance in a liquid, and the resulting mass is homogeneous throughout and fluid enough to form drops. This is not a perfect definition of a true solution, as will be seen when we further discuss the physical properties, but for the purposes of comparison and distinction between crystalloids and colloids it will serve ·for the present. Colloidal solutions will not meet the requirements of the above definition. Generally speaking, such solutions consist of two phases— a liquid phase which is the dispersion medium, and another liquid or solid phase which is dispersed as small particles in the dispersion medium. In colloidal solutions the particles are of finer grain than in colloidal suspensions. The degree of dispersity of the colloidal particles is, then, a matter of great importance, for if the dispersion is not great, we have emulsions and suspensions, while if the dispersoid is finely divided, we classify them as emulsoids and suspensoids. These terms have come forward within the past few years and are becoming more common daily.

A colloidal solution may be somewhat arbitrarily defined as a dispersoid in which the diameter of the particles ranges from 0.0001 to 0 000001 millimeters (usually written 0.1 μ and 1 0 $\mu\mu$) Mixtures with larger particles would be classified as coarse suspensions, and smaller particles would be found, of course, in molecular solutions.[5] Perhaps the most comprehensive definition of a colloidal solution would be as follows: a suspension, in a liquid medium, of solid particles (or liquid globules), the linear dimensions of which are approximately between the limits of 10^{-7} cm and 10^{-5} cm The lower limit is fixed by

[5] Herschel, in Alexander's "Colloid Chemistry," Vol. 1, Chemical Catalog Co., New York, 1926, p. 733.

the smallest particle yet seen by use of the ultramicroscope, while the upper limit is fixed by the size of particles which do not settle under· the force of gravity[6] Hence, a colloidal solution is a system of two or more mutually insoluble substances in which one exposes a great surface to the other The system shows specific characteristics not typical of suspensions only but approaching solutions. This would, of course, include finely divided pigments or other coloring matters which would resist sedimentation over an indefinite period.

It is customary to use the word "'microns" for particles exceeding a diameter of 250 $\mu\mu$ (visible in the microscope); "submicrons" are those particles ranging from 6 $\mu\mu$ to 250 $\mu\mu$ in diameter (visible in the ultramicroscope); and "amicrons" are the particles below 6 $\mu\mu$ in diameter, not visible in the ultramicroscope.

When a material is very finely divided and in permanent suspension, the dispersion medium may be solid, liquid or gaseous. In each case the mixture is called a dispersoid, and is of course heterogeneous. Herschel[7] has classified these mixtures into 8 types as shown in the following table :—

TYPES OF DISPERSOIDS

Type No.	Dispersed Phase	Dispersion Medium	Example
1..	Solid	Solid	Ruby glass
2	Liquid	"	Water of crystallization
3	Gas	"	Meerschaum
4	Solid	Liquid	Metals in colloidal state
5	Liquid	"	Emulsions
6	Gas	"	Foam
7	Solid	Gas	Smoke
8............ .	Liquid	"	Clouds

Modern work has shown that it is incorrect to speak of colloidal substances as a particular class. For instance, the alkali salts of the fatty acids, such as stearic, palmitic, oleic, etc., dissolve in alcohol as crystalloids with more or less normal molecular weights, but when dissolved in water they take no more of the colloidal behavior.[8] Paal[9] found that sodium chloride gave a so-called colloidal solution in benzol and when treated with petroleum ether it was precipitated out; while, of course, when it is dissolved in water, it goes into crystalloidal solution or in true solution. Von Weimarn has demonstrated by preparation of over two hundred chemical substances, including salts, elements, etc., that by proper manipulation almost any substance which

[6] E. F Burton, *ibid*, p 165.
[7] Herschel, *op cit.*, p. 732
[8] Krafft, Ber., 32, 1595 (1899).
[9] Paal, Ber., 39, 1436, 2859 (1906); 41, 51 (1908); 42, 277 (1909).

exists in solid state can be produced in solution, either colloidal or crystalloidal. In a large number of cases it is merely a question of concentration of the reacting components whether a crystalloidal or colloidal state results A salt which is readily soluble in water can be obtained in a colloidal state by working in a solvent in which the salt is practically insoluble, thereby precipitating it in an extremely finely divided state, when it takes on the properties of a colloid.[10] This virtually means that the same substance can be obtained in either state, depending upon the nature of the solvent. It is therefore better to distinguish between colloidal and crystalloidal states of matter rather than colloids and crystalloids.

The idea that the ultimate unit of a colloidal solution is not the molecule or ion of the solute, but an aggregate, has induced colloid chemists to consider this a new branch of chemistry in which the laws of classical chemistry are replaced by laws peculiar to the colloidal state of matter, which in reality is based on the laws of physical chemistry. Loeb[11] states that it was an unfortunate historical accident that the colloidal behavior of protein and other similar substances was investigated before the convenient method of measuring hydrogen-ion concentration; that if these principles had been applied in former years, the idea of the chemistry of colloids would not differ from the chemistry of crystalloids; and that it is this methodical error of not measuring hydrogen-ion concentration of colloidal solutions and gels which has retarded the development of an exact theory for colloidal behavior. This may be true in the case of proteins and such substances within narrow limits, but the ideas suggested along this line have not been favorably received by those specializing in this field. As Kopaczewski[12] has pointed out, considering the variety of chemical reactions which occur even with solutions of electrolytes (such as salt), it is no wonder that substances infinitely more complicated, as are colloids, in their nature and mechanism, should quite escape us. Nevertheless, we see from time to time attempts made to subordinate colloidal reactions and the properties of colloids solely to the laws of classical chemistry.

One of the clearest descriptions of the colloidal state of matter published in recent years was a paper presented by P. P. Von Weimarn[18] before the Russian Chemical Society, and the principles set forth at that time by Von Weimarn are so clear and concise that

[10] Bancroft, "Applied Colloid Chemistry," 2nd ed., McGraw-Hill Book Co., New York, 1926, p. 210
[11] Loeb, "Proteins and the Theory of Colloidal Behavior," 2nd ed., McGraw-Hill Book Co., New York, 1924, p 5
[12] Kopaczewski, in Alexander's "Colloid Chemistry," Vol 1, Chemical Catalog Co, New York, 1926, p 547
[13] Von Weimarn, *J. Russ. Chem. Soc*, 38, 466-470 (1906)

it is felt that it would not be out of place to quote from this paper to the extent of at least the essential points covered.

> By increasing the resistance to the forces tending to bring the particles into an arrangement characteristic of a crystal, we shall obtain any substance in the colloid state, conversely, on weakening this resistance, any substance will separate out in the crystalline state
>
> The colloid, the amorphous and the crystalline states are just as universal with matter as the property of matter is universal, to appear in the three states of aggregation, just as the realization of these latter states for all substances has ever required, and still requires, expenditure of time and effort, and also the application to the substance of more and more powerful agents, so is the preparation of all solid substances in the colloid, the amorphous and the crystalline states dependent on the same factors.
>
> For a given substance, no sharp boundary lines may be drawn between the colloid, the amorphous and the crystal states, since the mutual transition from one state to another is affected by degrees, as the resistance is overcome to the forces which tend to bring about separation of the substance in the crystalline state

These deductions were not a conjecture, nor were they a theoretical speculation. As a matter of fact, not alone was the idea of the universality of the colloid state embodied in these deductions, but they represented the *law itself* of the universality of the colloid state, established on experimental grounds.

In a communication read before the Russian Chemical Society during 1907, Von Weimarn [14] was able to show: first, that the colloid state must always be passed through, whenever already-existing phases disappear (*e g,* when substances dissolve, evaporate, and the like), and second, that particles (molecules and molecular complexes) similar in size to those present in colloid systems may, under some well-defined conditions also exist in such systems as are classed with the one-phase systems, according to the phase rule. Further quotations are given·

The Fundamental Principles of the Theory:

1 All the properties (both chemical and physical), which earlier were considered as specific for colloid substances appear spontaneously with *every* solid substance as its subdivision progressively increases, irrespective of the means by which this subdivision is brought about (*e g.,* whether they be chemical, physiochemical, physical, mechanical, and the like).

2. Any solid substance, regardless of what its chemical nature or any of its other properties may be, must always pass, on dissolving, through a *colloid stage of solution.* For the case of solid substances *rapidly* dissolving in the liquids selected, the time intervals during which the *colloid stage* of solution would persist will naturally be very small, but nevertheless, even for these cases, the existence of a *colloid stage of solution* is beyond any doubt

3. Any solid substance, regardless of what its chemical nature or any of its other properties may be, must always pass, on crystallizing, through a *colloid stage of crystallization.*

4 For *any* substance, such physico-chemical conditions of crystallization and solution may, according to one's wish, be realized at which the colloid stages of crystallization and solution would last for periods of time, of which the cor-

[14] *J. Russ. Chem. Soc.,* **39**, 391-619 (1907).

responding durations may be varied, according to the above-mentioned conditions, within extremely wide limits; *viz*, from fractions of a second and seconds, up to such large values as measured by years, decades, and even centuries

5 For *any* given solid substance, suitable solvents and such temperature conditions may be found, at which, in the solutions of this solid substance in the above solvents, large molecular complexes will form by way of solvation and association, subsequently to persist in a state of kinetic equilibrium, which (*i.e*, complexes) will not be inferior in size to the particles existing during the colloid stages of solution and crystallization of substances (*vide: Principles 2, 3, and 4*)

To the same species of the colloid state also belong solutions of solid substances, whose molecules contain *a large number of atoms condensed by ordinary chemical forces* (*e.g*, the proteins and the like), or—to put it in another way—the solutions of substances of composite chemical nature.

It is a matter of common knowledge that since the time of Thomas Graham and up to date, purely chemical interpretations of the colloid state of matter have never been wanting, resulting in the theory of "colloidal, chemically complex compounds" (the various "Complex" theories of colloids) and the theory of "gigantic chemical molecules," with the whole variety of its modifications.

My theory of the colloid state is neither "purely chemical" nor is it "purely physical." It is a "physico-chemical" theory and, therefore, it treats phenomena, whenever relevant, from either the physical or the chemical standpoint.

For further details of this interesting paper on the colloidal state of matter, see the complete presentation of this subject in "Colloid Chemistry," Volume 1, by Jerome Alexander.[15]

Kopaczewski,[16] who is in general agreement with Von Weimarn on this subject, states that the colloidal state is an intermediate one between suspension of solids governed by physical laws and true solutions governed by chemical reactions and the conditions under which the product is treated; such as examples given previously,—soap in water, soap in alcohol, sodium chloride in benzene and sodium chloride in water. This writer also agrees that the laws governing colloidal phenomena are not exclusively those of physics nor those of classical chemistry but an intermediate state responding to some extent to both laws

Many objections have been raised against the all-inclusiveness of the term colloid chemistry. To take its place other terms have been suggested, such as "capillary chemistry," "microchemistry," "chemistry of dispersoids," "chemistry of the realm of neglected dimensions." To eliminate such confusions Zacharias [17] proposed the term "metachemistry"; under this title should be considered all problems which are now classed in the various groups described above, just as the term "metaphysics" has in the past covered all uninvestigated processes. In this way workers would not be handicapped by the various hypothetical suppositions and the prejudice created through misunderstanding of the term colloid.

[15] Chemical Catalog Co., New York, 1926, p. 29-78
[16] Kopaczewski, *op. cit.*, p. 572.
[17] Zacharias, *Kolloid-Z.*, 36, 39 (1925).

It is quite evident that interest in colloids is growing rapidly and that new problems and new applications are being discovered at a very rapid rate. The conflicting points of view resulting from the complexity of the problems presented, and, not the least, the clashes over the nomenclature, all serve as arguments for more quantitative experimentation. Books on this subject in the future should help clarify at least the different states of matter according to the colloid viewpoint which undoubtedly will assist the research man in viewing the colloidal state of matter from the proper angle, and will assist greatly, of course, in solving the problems. As an illustration, this confusion is readily understood when we consider that very little systematic work has been done on sols and gels with liquids other than water. We really know very little about matter in the solid state. For instance, we know the shapes of the crystals and the forms. We know very little about the effect of various forms of energy, such as light, heat, electricity, when passed through solids, and even that which we do know is superficial In other words, our ignorance of the real nature of solids is almost perfect.

The theory of colloid behavior must be based on a knowledge of the forces acting on particles in solution These forces have been almost ignored and a new kinetic theory of solutions is, undoubtedly, needed. Preliminary attempts towards molecular theory of solutions have been made. On the other hand, atoms are no longer regarded as hard elastic spheres; instead, we believe them to be composed of positive and negative charges of electricity and that there is a force surrounding a residual field of force about each molecule through which all molecules attract each other, whether alike or otherwise. Larger particles consisting of several molecules possess smaller stray fields, which Bradford [18] states are approximately inversely proportional to the volumes of the particles.

It is believed (and in this there are a great number of workers of similar opinion) that there is a continuity of the liquid and gaseous states, that when a gas or vapor is at a temperature only slightly greater than the boiling point, it is not to be regarded as a collection of single molecules but must be supposed to consist of some single molecules and also of clusters of such molecules; [19] as this aggregation increases, the gas becomes vapor and shows the cloudiness of the critical stage, and droplets join into one mass and we have a liquid In a like manner, as the particles of a liquid decrease their kinetic motion, a state is reached where there is practically no motion and we have what is

[18] S. C Bradford, *Phil. Mag.*, **50**, 1142 (1925)
[19] J. H. Jeans, "The Dynamic Theory of Gases," 4th ed., Macmillan & Co, New York, **1925**, p. 200, *also* Von der Waals, "The Continuity of Liquid and Gas State," Leyden, **1873**.

called a solid. Of course, decrease in temperature decreases the kinetic motion. This gives the particles a chance to exert specific attraction so as to form larger aggregates.[20] This again diminishes the motion of the particles as their size increases, so that when we reach a size of about five microns, all motion practically ceases

What we commonly call the solid state is really a state of flux and slow internal readjustment. As stated by Washburn,[21] and also emphasized by Alexander, there are three classic states of matter; these are not gaseous, liquid and solid, but gaseous, liquid and crystalline.

We know more about liquids than we do of solids. For instance, we know the molecular weights of substances in the liquid state. The study of the physical properties of liquids has been very thoroughly dealt with, but even here what is known is comparatively little in proportion to what is not. On the other hand, the laws of gases are comparatively simple and well understood, for the reason that matter in the gaseous state lends itself to mathematical treatment in a way that no other state of aggregation does. In recent years it has become possible to deal with solutions by truly scientific methods, that is, the mathematical. This is due, in no small degree, to the relations pointed out by van't Hoff between solutions and gases, and since solutions lie at the foundation of all chemistry, there is no doubt but that progress has been made by the conversion of this branch of chemistry into a more exact science.

It is readily appreciated from a study of the colloidal state of matter, however, that this subject has not yet been worked out on such a simple basis, for whenever we find a property which changes with every change in composition of the substance and also with every change in its constitution, the study of such a property can only lead to empirical relations and these usually disappear as soon as enough facts are brought to light. Such phenomena cannot be expressed in continuous curves and we cannot deal mathematically with those that are discontinuous. This condition has held back the application of mathematics to colloidal chemistry and has kept it longer in the condition of an empirical branch of science, for the numerical properties may be called the fundamental ones and it is investigation of these constant properties which really advances the science.

[20] Alexander, "Colloid Chemistry," Vol. 1, Chemical Catalog Co, New York, 1926, p. 18.
[21] E W. Washburn, "Principles of Physical Chemistry," 2nd ed., McGraw-Hill Book Co., New York, 1922.

Chapter II.

The Colloidal State of Matter from the Physical-Chemical Viewpoint.

The researches of physical chemists show that there are *degrees* of solution, and that no marked division exists between true solutions and colloidal solutions, nor between colloidal solutions and suspensions. In other words, one merges into the other without any definite dividing line. The chief distinction between colloids and crystalloids lies in the nature of the forces by which the two kinds of substances are kept in solution (in water or in other solvents). The forces which determine the stability of crystalloids are those of a chemical nature, the molecules of the solute and solvent being attracted to each other by chemical affinity or so-called secondary valency forces.[1] As long as the attraction between the molecules of the solvent and solute is great enough, the solution will be stable. When such forces become too small, aggregates of molecules are formed. These may remain in suspension, however, provided a difference in potential is established between each particle and the solvent. We now no longer have a true solution but a colloidal solution, that is, a suspension, and the forces which guarantee the stability of such a colloidal solution or suspension are those of electrostatic repulsion. It is believed that there exists at the interface between each particle and the solvent a double electrical layer, thus creating a difference in electrical potential This will be discussed more fully, but it is necessary to point out at this time that in all fine dispersions such conditions are believed to exist.

Emulsions are more like true solutions than are suspensions. While they are, in a way, suspensions, they are more readily adsorbed and are more capable of entering into chemical reactions with one another In fact, it may be said, in general, that when a suspension is added to an emulsion, the system usually takes on the properties of the emulsion, this is probably due to the emulsion forming a coating around the suspension and thereby giving the characteristic properties of an emulsion

[1] Loeb, "Proteins and the Theory of Colloidal Behavior," 2nd ed, McGraw-Hill Book Co, New York, 1924, p 10

PROPERTIES OF COLLOIDAL SOLUTIONS AS COMPARED WITH TRUE SOLUTIONS

In order to understand the differences and dividing lines between so-called colloidal solutions and true solutions, we must deal briefly with some of the most characteristic properties of each type from the physical-chemical viewpoint.

The three most characteristic properties of true solutions are osmotic pressure, lowering of freezing point and the rise in boiling point. These properties are characteristic of all true solutions and they obey definitely defined laws. The osmotic pressures of true solutions obey the laws of gases. The lowering of the freezing point of the solvent, as well as the rise in boiling point produced by dissolving a substance therein, is in accord with the well-known laws of Raoult. How can it be determined that a system which appears to be a true solution is in reality a true solution? Of course the answer is, by determining its concentration, its osmotic pressure, its freezing point and its boiling point, and determining whether all of these conform to the laws for the state of true solution.

The question now naturally arises: do colloidal solutions have these three characteristic properties? As pointed out by Bancroft,[2] we should not expect a coarse suspension, if entirely insoluble and anhydrous, to give rise to osmotic pressure, and as diffusion is brought about through osmotic pressure, we should not expect it to show any properties of diffusion except as a result of electrical charges. While this is true practically, it is not so theoretically. Einstein[3] claims to have shown that according to the molecular kinetic theory the colloidal solution should give rise to osmotic pressure and diffusion just as ordinary solutions, and there is no difference between a suspended particle and a molecule. The diffusion of colloids through membranes such as parchment is practically nil, while crystalloids readily pass through when in solution. Therefore, by the method of dialysis a mixture of colloids and crystalloids may be separated. In natural colloids, however, the mineral constituents are closely bound into the product and for the greater part do not diffuse away. In other words, the mineral constituents must be regarded as constitutional.

The freezing point lowering and the lowering of vapor tension or the rise of boiling point produced even by emulsoids must of necessity be small, since the osmotic pressures are very small, when one considers that an osmotic pressure of 1 mm. of mercury corresponds to only about one ten-thousandth of a degree lowering of the freezing

[2] Bancroft, "Applied Colloid Chemistry," 2nd ed., McGraw-Hill Book Co, New York, 1926, p. 225-226

[3] Svedberg, "Colloid Chemistry," Chemical Catalog Co., New York, 1924, p. 92.

point. Bruni and Pappada [4] prepared very pure sols of albumin, gelatin, and other emulsoids and were unable to detect any difference between their freezing and boiling points as compared with those of pure water. This tends to show how meaningless are the number of attempts that were made to determine the molecular weight of colloids by the boiling and freezing point methods such as is done in the case of crystalloids.

SUSPENSION AND EMULSOID COLLOIDS

Colloids are frequently divided into suspension colloids and emulsoid colloids. This division is made due to the fact that, generally speaking, the suspension colloids do not add appreciably to the viscosity of the medium in which they are dispersed (which may be water or some other liquid). They also are readily precipitated by the addition of electrolytes such as acid, alkali or a salt.

EMULSOID COLLOIDS

The emulsoid colloids are characterized by having more of a swelling effect, probably brought about by imbibing water more or less before dissolving to any great extent. An example of such a colloid is gelatin, which will absorb about six or eight times its volume of cold water without showing signs of dissolving. Another example is gum tragacanth, which is said to absorb forty times its own weight of water. Another good example is Bentonite (colloidal clay). Of course, this absorption is accompanied by a great swelling action. Some of the colloids, such as albumin and gum arabic, appear to dissolve readily in cold water, these probably approach close to the crystalloids in type. Others, such as starch, gelatin and agar, are dissolved by heating

The fact that crystalline egg albumin and gelatin require high concentrations of electrolytes to precipitate them has led some authorities to suggest that such proteins form emulsions instead of suspensions, such as clay or graphite would do, and require only low concentration of salts to precipitate them. It therefore became customary to classify the substances which require high concentration of salts for precipitation as emulsoids and those which required low concentrations of salts as suspensoids. Genuine proteins were all classified as emulsoids. As pointed out by Loeb [5] and shown by Powis, [6] true emulsions of oil in water are flocculated by the same low concentration of the salts as are the solid particles in suspension, and the so-called emulsoids behave like crystalloids with regard to solubility but are not really like emulsions in their dispersion.

[4] Bruni and Pappada, *J. Chem. Soc.*, —, 87 (1906).
[5] Loeb, *op. cit.*, p. 13.
[6] Powis, *Z. phys. Chem.*, 89, 91, 179, 186 (1914).

The so-called emulsoids, such as gelatin, casein, albumin, are often spoken of as hydrophilic colloids because they readily take to water, that is, they easily adsorb water and are easy to disperse. Some of them are soluble in cold water, while others require slight heating or sometimes a trace of alkali, such as in the case of casein The suspensoids, on the other hand, are sometimes classified as hydrophobic colloids because they do not readily take to water and require dispersion, usually with some sort of a protection, such as an emulsoid colloid. The suspensoids, of course, are products such as clay or graphite dispersed in water.

FILTRATION

In a true solution the molecules readily pass through any filter medium, whereas particles in suspension are retained by the filter unless extremely fine. In using filter papers, the pores are chosen according to the material to be filtered These pores vary in size in the different qualities of paper A colloidal solution will go right through an ordinary filter. Bechold.[7] has shown that it is possible to form a colloidal film on such filters and he has obtained pores of almost any desired size With the more porous filters the finer particles go through, while the coarser ones are held back · In this way it is possible to get an approximate idea of the relative size of particles in two different colloidal solutions. This would be classified as ultrafiltration

For some purposes filter cones of porous porcelain are employed Bechold gives the following figures as to the sizes of the pores in filter media:

	Average Size of Pores	Size of Largest Pores
Ordinary thick filter paper.......	$3\,3\mu$	......
Schleicher & Schull's filter paper, No. 556...... ..	$1\,7\mu$	. .
" " ". extra hard	0.89–$1\,3\mu$	1–$1\,5\mu$
Chamberland filter ,...	.... .	0.23–$0\,4\mu$
Reichel filter	......	0.16–$0\,175\mu$
Puckall filter	0.2–0.4μ	......

In filtering colloidal fluids, if the aggregates or micelles are of considerable size they attach themselves to the fibers, hence the pores of the filter soon become clogged and the passage of the liquid, of course, becomes slower and is finally stopped altogether Therefore, filtration is not a simple operation, governed by the size of the particles as relative to the pores of the filter medium.[8] To illustrate, powdered lampblack when shaken up with water cannot pass through the ordinary filter paper, and the water will come through clear; but if a small

[7] Bechold, *Z. phys. Chem*, **60**, 257 (1907).
[8] Bancroft, *op. cit*, p 219

amount of a protective colloid, such as soap, is added to the water, the lampblack will readily pass through the filter, especially if the soap concentration is kept fairly low. In other words, the soap will form a protective film around each particle, offsetting the flocculation so that it can readily pass through the filter.

This flocculation is probably brought about by the fact that when lampblack is in contact with water both have a weak negative charge. When soap is added, hydroxyl ions are absorbed by the filter and the lampblack and they become more negative. This increases the like charge sufficiently for the filter paper to repel the lampblack while it passes through the pores. This phenomenon is also reported when paints are diluted with benzene and filtered. This question of charges will be more fully dealt with in Chapter VI.

SURFACE TENSION

Acting counter to the stability brought about by like charges on colloidal particles we have surface tension. The action of surface tension is to draw the object into the smallest possible volume for a given mass. A good example of this action is mercury, which, when thrown upon a table, forms little spherical particles. In colloids, surface tension tends to draw the small groups together, forming larger particles which are the units of clots or precipitates. The surface tension varies greatly with the liquid. To illustrate, the surface tension of ether is far less than that of water, while that of mercury is much greater.

When two immiscible liquids are in contact with each other, the surfaces of these two liquids are under tension. The tension between these two phases is known as interfacial tension and the liquid with the greater surface tension of course will have more of a tendency to draw itself into the smallest possible volume, hence tends to take on the spherical shape. (This will be dealt with more fully in the discussion on emulsification.)

Where the surface of the fluid is in contact with air, a true measurement of surface tension is obtained. This can be gauged by measuring the size of the drops which form as the liquid issues from a capillary orifice, also by its rise in a capillary tube. In dispersion and emulsification, the important factor is the interfacial tension between the two liquids at the point of contact. This can be measured by the size of drops which form when one of the liquids is allowed to pass through a capillary tube below the surface of the other liquid and the number of drops counted from a measured quantity of the liquid. It can be determined by means of what is known as a Donnan drop pipette.[9] If this pipette is filled to a definite capacity with some liquid such as tur-

[9] F. G. Donnan, *Kolloid-Z.*, **9**, 208 (1911).

pentine and the orifice submerged below the surface of distilled water, the number of drops of turpentine from this known volume through the pipette is counted   If this experiment is repeated, but to the water is added 1 per cent of potassium oleate or other soap, it will be found that in the soap solution the drops are smaller and, therefore, more numerous from the same volume of turpentine. The soap, therefore, has lowered the interfacial tension between the water and the turpentine. The question of interfacial tension, then, is most important in all work on emulsification, and is of great assistance in classifying emulsifying agents as to their value in lowering surface tension.

Since liquids and vapors are identical at their critical temperature, the surface tension of pure liquids decreases with rising temperature until it reaches the boiling point, when the surface tension becomes zero. This is an important factor in problems in connection with emulsification.

The change in surface tension when a film is formed is most important, as the surface film of a liquid has a different concentration from the mass of the solution. The concentration in the film tends to change so as to decrease its surface tension [10] Consequently, the surface film will be more dilute than the mass of the solution if the dissolved substance increases the surface tension, and will be more concentrated if the solute lowers the surface tension of the solution. A very convincing demonstration of this point is brought about by dissolving a small quantity of any water-soluble dyestuff and adding to this solution a small quantity of some product, such as gelatin, which will lower the surface tension; the solution is then agitated and some of the foam removed from the top. If this foam and an equal weight of the original solution (without gelatin) is added to cylinders containing equal volumes of water, it will be noted that the water, to which the foam has been added, will be much deeper in color than that to which the equal weight of solution was added. In other words, the decreasing of the surface tension in this instance has caused the soluble dyestuff to concentrate more in the foam phase than in the liquid itself.

When sodium oleate or any such surface-acting colloid is added to another more inert colloidal solution, such as a pure serum, the surface tension is decreased considerably and then rises again and may reach its initial value in about seven minutes [11] Generally speaking, soaps lower the surface tension between water and oils so that quite permanent emulsions are sometimes made up in this manner. The washing power of soap, as well as its wetting power, is dependent to a great extent upon this lowering of the interfacial tension. These effects become more pronounced as we increase in the fatty acid series. Such effects

[10] J. W. Gibbs, "Scientific Papers," 1, 219 (1906).
[11] Bancroft, *op. cit.*, p 152.

are limited, however, and the maximum effects are usually produced with between 0 3 to 1 per cent of soap in solution.

In an emulsion of the oil-in-water type, when the interfacial tension between the two liquids is lowered the colloidal sols migrate to the interface, and the oil globules become coated with a thin film of the colloidal material which is less hydrated than that in the surrounding medium and which prevents the coalescence of the oil globules. The presence of these films can be demonstrated by dissolving the oil with the proper solvent, when the empty shells will be visible for a short time, particularly with a coarse emulsion. With very finely divided mineral matter in permanent suspension the same phenomenon results

Even solids probably have a definite surface tension, and the melting point of the solid might be considered as that point at which the surface tension overcomes the crystalline forces.

Examination under the microscope proves that so-called homogeneous fluid systems, such as air, water, etc., actually contain an enormous number of minute surfaces. These surfaces, therefore, form the outside of every phase or particle, and if a thermometer is used to take the temperature of a liquid, its bulb must first be put through the surface. In vaporization, all molecules must jump from the surface of the liquid, and the condensation of vapors also occurs upon the surface. If two particles unite, the surface disappears, and if divided, their surface reappears. As pointed out by Harkins,[12] it is evident that surface energy is one of the most fundamental properties which distinguishes colloids from other systems. If water is dropped upon a hot stove, a vapor film is formed about the spherical particle, and it acts as a cushion until the temperature becomes too great. Very dry dust probably assumes the spherical shape. This suggests, therefore, that every liquid is surrounded by an elastic film, the tension of which causes the surface to contract to the smallest possible area for the volume of the liquid, provided there are no other forces to counteract this, such as the action of gravity, etc. We see this action of surface tension almost any way we turn, such as water dropping from a faucet, the rise of liquid in a capillary tube, the submerging of a camel's hair brush into water where the hairs will remain spread apart but when the brush is removed from the water the surface tension will bind the hairs compactly together.

If the state of a system is changed, the system will alter in a way to offer a resistance to such a change, as stated in the rule of Le Chatelier,[13] and since the surface tension decreases with the temperature, a surface must cool if it is expanded, since by cooling, the surface

[12] W. D. Harkins, in Alexander's "Colloid Chemistry," Vol. 1, Chemical Catalog Co, New York, 1926, p 192.
[13] Harkins, *op. cit.*, p. 195, 196.

tension is increased and this gives an extra resistance to the further expansion.

SURFACE ENERGY

In order to appreciate fully the importance of surface tension in the study of colloidal dispersion, and especially so in the case of any investigations pertaining to emulsions, it is a decided advantage to have in mind the principles of thermodynamics, considering kinetic energy, or that which is active, and potential energy, which of course is that in storage or that which is released when the occasion demands. In the vaporization of a liquid the kinetic energy of molecular vibration of the molecules in the liquid is converted partly into potential energy, or the molecular energy of motion is utilized in the separation of each molecule from its neighbor. As this is an effect offsetting the tendency of the various molecules to flocculate or group together, it is a point in favor of stability, and it is the molecular vibration of these molecules which determines the temperature A molecule in the interior of a liquid must have sufficient energy when it moves into the surface to do so against the attraction of the surrounding molecules, and of course it must move into the surface before entering the vapor phase. If it has sufficient kinetic energy to reach the surface, then the additional energy which it has would remain as potential energy, and help to hold its relative position in the surface, unless there is additional kinetic energy, when it would enter the vapor phase. In other words, when a surface is formed on a definite liquid at a definite temperature, a definite amount of energy must be contributed and converted into potential energy.

Harkins [14] has explained this principle in a manner readily understandable by anyone, as follows: "Whenever a molecule moves from the interior of a liquid into the surface in such a way as to form a new surface, the average amount of its kinetic energy which is converted into potential energy is equal to 144 per cent of the mean translational kinetic energy of a gas molecule at the same temperature." Therefore, only the faster-moving molecules possess sufficient kinetic energy to carry them into the surface and all known surfaces have a positive free surface energy. From this we gather that the molecular potential energy in the surface molecules is always greater than 144 per cent of the mean kinetic energy of the molecules of the mass.

Atoms at the free surface are attracted inward, whereas the attractive forces acting on an atom in the interior are distributed over the whole circumference of the sphere. Therefore, it is easy to recognize that there is an excess of attraction at the surface, the .total potential

[14] Harkins, *op. cit.*, p. 196.

of which with the excess heat in the surface layer constitutes surface energy.

As pointed out by Harkins,[15] a colloid is distinguished by the fact that the surface or interfacial energy has a value which is an appreciable fraction of the molecular energy of the dispersed phase. Harkins illustrates this point through a simple calculation which shows that
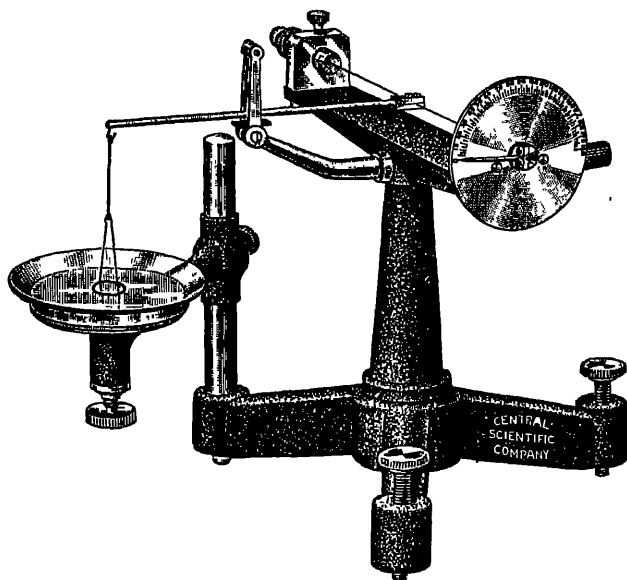
Fig. 2.—Apparatus for Measuring Surface Tension
Courtesy of Central Scientific Co

when one cubic centimeter of water is sprayed into spherical droplets 0.01μ in diameter, the superficial area of such droplets is about 6,000,000 square centimeters and the free surface energy for this area at 20°C. would be 218,000,000 ergs or 10 5 calories, the total surface energy would be 16.6 calories, which is calculated to be one-third as much as the kinetic energy of vibration of the water molecules These figures are of interest in showing the importance of surface energy.

With liquids heat exerts a marked dispersing action, diminishing the size as well as the number of the aggregates with a corresponding increase of the dispersed phase This is similar to dilution of the dispersion and the reduction of the percentage of the dispersed phase In the case of solids, heating does not show any visible effect, except

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[15] *Op. cit.*, p. 192.

expansion, until the atomic or molecular swelling, due to the increased kinetic motion, becomes great enough to permit particular kinetic activity At this point, the attraction of the individual molecules for each other is not as great, and due to this additional kinetic activity of the molecules, or groups of molecules, the solid is then in a state of fusion, in other words, it is a semi-liquid and at this point a slight increase in temperature, or excess agitation, makes it pass over to the fluid state

In the course of the change from the region where the specific surface is dominant to that where kinetic motion is dominant, we must pass through a zone where the two factors are nearly balanced, where increasing specific surface shows its effect before the kinetic motion is violent enough to reduce the surface attraction factors to a relatively less important level. This region is known as the colloidal zone of dispersion, and properties such as viscosity should reach their maximum where the dominance of specific surface ends and that of kinetic motion begins. This zone has been termed by Alexander [16] the "zone of maximum colloidality." It was first observed experimentally and its theoretical explanation given after observations had been made of such a condition existing.

When sugar is dissolved in water this solution has less free energy than the separate solid and liquid phases. On the other hand, when we have colloidal gold dispersed in water, this sol has an excess of free energy compared with the separate phases. As the free energy tends to a minimum, the surface energy tries to lessen that of the surface of the dispersed particles by attaching these particles one to another, or by coagulating the colloidal solution.

Since, in colloidal dispersions, the coagulated system is more stable than the sol, why is it that the colloidal system exists at all? Why does not the free surface energy cause immediate flocculation or coalescense of the particles? In the first place, in order for the particles to flocculate or coalesce, it is necessary that they collide. Preventing this possibility of collision we have the charged particles to consider. If these particles all carry a like charge, it is a factor in favor of stability, while acting counter to this is the surface tension action which is against the conditions for stability as above described. Hence, we must consider all of these factors before coming to a hasty conclusion.

BROWNIAN MOVEMENT

There is another most important factor to consider and that is what is known as the Brownian movement of the particles. This is a factor against stability in case of emulsions and it is largely due to this that it is necessary to have a protective colloid so that when the dispersed

[16] Alexander, *J. Am. Chem. Soc.*, **43**, 434 (1920).

particles collide, coalescence does not follow. These are spoken of as emulsifying or stabilizing agents and are supposed to form a film about the dispersed particles so that when they become within the zone of attraction of each other, this skin or film protects them from coalescence, or in the case of solids from flocculation

The English botanist, Robert Brown, observed as early as 1827 that pollen grains of plants when suspended in water were in a continual state of oscillatory motion. Brown [17] was making a microscopic study of the grains of pollen from *Clarckia Pulchella* and observed that they moved about in the liquid. Further experiments by Brown [18] showed that very finely divided solid particles suspended in any liquid which was not too viscous showed the same movement, and Brown considered that he was watching the movement of active molecules. These very finely divided solids do not settle at all. They seem to neutralize the action of gravity more or less completely. These early experiments of Brown were a clue to this important point, but his experiments were not appreciated until very much later.

The very elements of the principles of thermodynamics go to prove that matter in all its stages is in motion. For instance, in gases the molecules are all in very active motion. They have great distances to travel before colliding with another molecule, or in more scientific terms we say their mean free path is very great. When these gases are condensed to a liquid, the molecules are more closely packed together and their mean free path is not so great. As the molecular motion is further decreased by lowering of temperature, we finally reach a condition of matter where this motion is very slight; this is often designated as the solid state. As this solid is again heated, the molecules increase their vibration, which is the factor governing the rise of temperature, and we have the reverse condition up to the gaseous.

Suspension of very fine particles or fine-grained emulsions and colloidal solutions of metals all show, when examined under the ultramicroscope, that the particles of the dispersed phase are in a continuous zigzag motion. .The phenomenon today is spoken of as Brownian motion, after Brown, who studied the movement of pollen grains in water. It is now known that the movement of these finely divided particles or suspensions in liquid is due to the bombardment of the particles by the molecules of the surrounding liquid, which, of course, are in constant motion, as explained under the subject of Surface Energy (p. 26). This Brownian movement is not observed before the particles are split to a very finely divided state. While it starts at a particle size of about 5 μ, it is more readily observed at 2 μ or less

Many points are explained by the Brownian movement. For in-

[17] R. Brown, *Phil. Mag.*, 4, 161 (1828); also *Pogg Ann.*, 14, 294 (1828).
[18] R. Brown, *Phil. Mag.*, 6, 161 (1829).

stance, Brewer [19] points out the slow rate at which clays settle, and raises the question whether extremely finely divided particles really settle. We now know that sufficiently finely divided particles will be kept in suspension in a liquid indefinitely by the Brownian movement, provided, of course, that coalescence or flocculation is prevented Such a colloidal solution is usually designated as a sol, and in practice it is commonly stated that when particles are dispersed to the size of about one micron they will not settle This, however, depends upon the viscosity of the liquid in which the particles are dispersed.

Since the bombardment of the molecules of the dispersion medium tends to diffuse the particles dispersed therein, we may get diffusion of fine dispersions through the action of Brownian movement. This action tends toward uniform distribution of the suspended particles, provided it is not interfered with by surface tension, electrical stresses, etc. As this movement is due to the incessant motion of the molecules of the fluid in which the particles are dispersed, the finely divided particles distribute themselves fairly uniformly. While a particle in suspension in a liquid is always acted upon by gravity, the buoyant force of the medium, the action of the Brownian movement, and the resistance due to viscosity must not be overlooked. If the magnitude of the Brownian motion happens to be equal to or greater than the vertical motion due to gravity, the latter will be completely offset and the particles will cease to show any settling over long periods. From the conditions of temperature and density of particles it is possible to calculate the critical radius of a spherical particle such that the Brownian movement for a given period of observation is just equal to the gravitational fall during that period.[20] As a general rule, if the particles are kept below 0 5 μ they will remain in suspension indefinitely through the action of the Brownian movement, so long as the particle remains in such fine division If two or more of these particles coalesce or flocculate, the force of gravity may cause them to settle

The velocities with which the particles move are also a function of their size Exner [21] showed that particles ranging from 0 4 to 1.3 μ move with a velocity of from 3 8 to 2.7μ per second, while very much smaller particles as examined under the ultramicroscope move with velocities as much as thirty times greater Temperature has a great effect; Exner has shown that between 20° and 70° C the square of the velocities is proportional to the temperature As the Brownian movement is due to the impacts or blows of the molecules of the liquid against the solids suspended therein, Einstein reasoned that if large

[19] Brewer, *Am. J. Sci*, 29, 1 (1885)
[20] E. F. Burton, in Alexander's "Colloid Chemistry," Vol. 1, Chemical Catalog Co, New York, 1926, p. 166.
[21] Exner, *Ann. Phys.*, 2, 843 (1900).

molecules such as cane sugar and the like in true solution obey the gas laws, then there was no reason why the grains of an emulsion should not obey these laws. It is impossible at this time to dispute this point but we can safely say that in order to conform with the gas laws, the particle size of the emulsion dispersion would have to be very minute and practically down to the size of molecules, which is rarely the case in practice.

Ehrenhaft [22] was the first to carry out direct measurements of Brownian movement of particles in gases. He found that there was a much livelier motion of these particles in gases than in liquids. At the same time the action of gravity on the particles is much more apparent in gases than in liquids, which would be natural to expect due to the buoyancy of the liquid. He observed that the comparatively large particles in the smoke of cigars, cigarettes, etc., as well as in the fume of ammonium chloride, had a Brownian movement, and with smaller particles obtained by spark discharging between zinc and platinum electrodes he was able to prove the existence of motion in gases completely analogous to the Brownian movement in liquids

As the size of the particles becomes less than 10^{-5} cm the molecular bombardment by gas molecules, to which they are subject, becomes more effective, and the particles stagger about the gas in response to the impacts of the gas molecules. As the size of the particles becomes further diminished, the influence of gravity becomes less and the molecular impact greater until the path of the particle resembles that of a football in play, but in three dimensions instead of two [23] Ehrenhaft found that particles larger than the mean free spaces of the gas (1×10^{-5} cm.) fell in zigzag lines because the velocity due to gravity was greater than that due to molecular impact   With smaller particles, down to 1×10^{-7} cm., the velocity due to molecular impact is greater than that of gravity, and the particles remain in Brownian movement in the gas, this movement increasing rapidly with the smaller particles

$$\tfrac{1}{2} M V^2 = K = \tfrac{1}{2} m v^2$$

$M =$ mass of particle	$m =$ mass of gas molecule
$V =$ velocity of particle.	$v =$ velocity of gas molecule

From the above calculation, one will note that the velocity of Brownian movement of any particle is inversely proportional to the square root of its mass and at a given temperature this velocity is the same for any particle of a given mass, whether it is suspended in a liquid or in a gas   It has been calculated that at normal temperature and pressure the mean free path of a molecule in a gas is hundreds of

[22] *Sitzungsber Akad Wiss. Wein,* IIa, 116, 1139 (1907)
[23] W E Gibbs, in Alexander's "Colloid Chemistry," Vol 1, Chemical Catalog Co, New York, 1926, p. 405.

times longer than that of a molecule in liquid. Hence, the length of the mean free path described by a particle between two consecutive impacts when suspended in gas is much greater than when it is suspended in a liquid, so that the distance the given particle travels in a gas over a definite period is much greater than a similar particle in a liquid at the same temperature. The general effect of this greater amplitude of Brownian movement in gases is to delay settling and promote diffusion.

Chapter III.

The Elementary Structure of Matter.

THE ELECTRON

None of the newer theories of chemistry or physics has claimed the attention of, or has been so fascinating to the scientist, in recent years, as the results of the study of the electron and radioactivity.

The electron is not only regarded as the structural unit of matter, but the derivation of elements from lower to higher in atomic weight is explained as due to the number of electrons. The forces which cause units of matter to associate or combine, may, therefore, be traced back, in all cases, to those of electrical origin. It has been customary heretofore to speak of chemical forces and physical forces as if one were dealing with chemical reaction, such as that between sodium carbonate and hydrochloric acid, or a physical reaction, as in the case of solution of common salt or sugar. These lines of demarkation, however, are now being largely broken down, and it is beginning to look as if the subject of physical chemistry covers the entire field and that one really overlaps the other.

Since atoms consist of particles which are either negatively or positively charged, all surfaces are made up of electrical charges because the electrons form the outer part of the surfaces. However, the relative position of the electrons is not thoroughly understood as yet, and we usually say that a surface is charged only when there is more electricity in it of one sign than corresponds with electrical neutrality.

The smallest material units whose existence has thus far been discovered are what are known as the protons, which are individual particles of positive electricity. These are, in turn, surrounded with negative particles of electricity known as electrons, and they go to make up what are known as chemical elements.[1] The size of the electron has been accurately measured by Millikan.[2] To give some idea of this —the number passing in a single second through an ordinary incandescent bulb is so large that it would take two and one-half million people, counting continuously at the rate of two a second, about twenty thousand years to complete the task. Evidence indicates that the proton, or

[1] Millikan, "The Electron," University of Chicago Press, Chicago, 1924, p. 182.
[2] Millikan, *op. cit*, p. 111, 121.

positive electron, is smaller than the electron, which is the term usually designated for the negative charge. However, the proton is much greater in mass or weight.

The size of the electron is perhaps better realized by taking Bohr's comparison [3] of the chemical atom with a miniature solar system, the nucleus or sun being the proton, which is surrounded by the planetary electrons. The electrons are relatively so remote from the proton or nucleus (in proportion to their diameter) that this comparison in ratio seems to be quite apt.

It has also been discovered within the last few years that the behavior of an atom is dependent upon the exterior layer, that is, the outer ring or shell of electrons, which are supposed to be rotating about the nucleus or proton similar to a solar system. If the atoms are made up in this manner—as all evidence seems to indicate they are—and these start with positive and negative charges of electricity, it is very logical that we should expect, in the study of colloidal dispersion, which is groups of matter in suspension, that we have to deal with these electrical properties which are passed from the electron through the grouping of particles into the micelle; this is what we picture the colloidal state of matter to be The rapid rotation of the electrons about the positive nucleus prevents them from falling in and offsetting the attraction of the positive proton. Chemical reactions seem to be modifications of electronic motion.

While the above may be considered by some to be a theoretical discussion, and not practical, it might be called to their attention that the former chemical definition of substances gives no explanation of their properties or structure For instance, the formula SiO_2 does not explain the color of mountains, and the symbol C does not explain why a diamond may be blue, black or colorless. This new development in science will eventually take us away from the habit of establishing decisive divisions between the various states of matter, and will, undoubtedly, lead to simplifying some of the sciences to a great extent. From present indications it appears that a great amount of the unknown in colloidal chemistry will have to be determined from this angle.

To demonstrate what is meant and why we should go clear back to the electron to trace matter up to the colloidal state, it is most advisable at this time to cite the different orders of complexity, as outlined by Alexander.[4] First, the atom is believed to consist of positive and negative charges of electricity, from which all substances are built or grouped. The negative charge of electricity is known as the electron, while the positive, as previously stated, is known as the proton The

[3] Bohr, *Phil. Mag*, **26**, 1476 (1913) , **30**, 394 (1915)
[4] Alexander, "Colloid Chemistry," Vol 1, Chemical Catalog Co, New York, 1926, p. 12, 13.

electrons revolve about the protons, similar to a solar system, and make up the atom, therefore, the atom is a "highly complex unit" and classified as a "complexity of the first order."

The number of molecules formed by combinations of atoms is enormous. The molecules are, of course, larger and more complex than their component atoms. These are the chemical compounds and they may be termed "complexities of the second order."

The residual attractive forces then express themselves by forming relatively small molecular groups. These molecular groups vary in size and duration of existence, according to the temperature, pressure, impurities present, and other such conditions. For instance, it is frequently stated that ordinary water is mainly a grouping of the molecules and not the straight H_2O, as formerly thought. In some instances these molecular groupings become irreversible and we have what is known as polymerization, with formation of new and larger groups; in fact, the formation of solids from liquids may be considered as a general aggregation of molecules. These molecular groups may be considered as "complexities of the third order"

The physical size of the molecular groups depends, of course, largely upon their component molecules, as some molecules are so large that they enter within the limits of the ultramicroscope and are visible. For instance, the molecule of starch is supposed to be 5 millimicrons in diameter. Primary colloidal particles of this nature are "complexities of the fourth order."

In some cases these primary colloidal particles way form groups and still maintain their individual identity, although bonded together by various forces. These can be classified as "complexities of the fifth order."

Up to this point the materials or units have been considered below the limit of the microscope, for they are smaller than the wave lengths of light, therefore could not be seen by any present optical means except by what is known as dark-field illumination, in which they reflect sufficient light from rays penetrating through the side of the field so that they can be seen by a high-powered microscope, this combination being known as the ultramicroscope. Where these are visible through such a microscope, they might be classified as "complexities of the sixth order," and if such groups are increased enough to be seen with the ordinary microscope, they may also be classified as complexities of the sixth order.

If these particles group into larger clusters, the microscopic particles may become large enough to become visible to the naked eye. These would be classified as "complexities of the seventh order."

A great number of the ordinary working properties and qualities of matter depend upon its finer structure rather than its chemical anal-

What we call black is in reality the complete absorption of light which causes a contrast with other materials which have not this property. Pulverized silver is black because the crystals are arranged in such a manner that the light is absorbed by reflection back and forth between the particles. The same effect can be brought about by taking a series of steel needles with their points placed together in a bundle. When observed, the mass will appear black, for the same reasons as in the case of pulverized silver.

Various colors on fabrics are due to the absorption of various wave lengths or the absorption of the various colors of the spectrum, the others being reflected and giving the color effect. By properly arranging fibers in a cloth or fabric so that some absorb light more than others, we can get various color effects. Various thicknesses of glass and other materials will cause varying degrees of absorption and bring about different colors, such as light passing through a prism (due to the difference in refraction of the various light waves) producing the color effect. Which, of course, is pronounced in the case of a glass prism.

If a number of straight lines are ruled parallel and set very closely together on a smooth surface, they will spread a ray of light out similar to the condition in a prism, this is known as a diffraction grating. We have similar conditions in fine drops of water or particles of dust on glass. In the case of agate, which is composed of thin films of about 0.001 mm. thickness, these films act as the diffraction grating when the agate is cut in cross-section to the films. The same conditions exist in mother of pearl, where layers of calcium carbonate and an organic substance known as chitin alternate in layers.[7] These are all a matter of structure, giving the various color effects.

Again, if we take a thin film of light reflected from the front and back of a surface, such as plate glass, it sometimes happens that the crest of some of the waves reflected from the surface will coincide with the hollow of the waves reflected from the other surface. In this case this particular color, that is, the wave length concerned, disappears, and where this occurs we get the complementary color. The colors, for instance, of soap bubbles, oil films, tempered steel, lead skimmings, and the wings of certain insects, are all illustrations of this color effect, which is brought about through thin plates or films and is entirely a matter of structure. The colors on carborundum are due to thin films of silica. Also the colors on a great number of the feathers of birds are due to the thin films and is not actually pigment.

Colors of various waters are believed to be due largely to suspended matter, in a great number of instances a suspended calcium carbonate. It is claimed that the blue of the Gulf Stream is due to the

[7] Bancroft, *op. cit.*, p. 247.

fact that there is less carbon dioxide in the water and consequently less calcium carbonate.[8]

The degree of fineness is, of course, an important factor. As an illustration of this, certain effects in photography can be obtained by regulating the fineness of the precipitated silver on the photographic plates.[9]   There are a great number of colors brought about through surface reflection, and this is due, to a great extent, to the structure from which the light is reflected.

Very little is known about the colors of the various gems.   In many cases the colors are affected by heat, expansion in some way changing the structure.   Also, when some of the gems are placed under various lights, entirely different colors are obtained; for instance, colorless topaz becomes yellow or orange after treatment by radium, and when heated it becomes colorless again.   Hence, the action of short waves on gems gives some very peculiar results.   The color effects, when treating with ultra-violet light, x-ray and radium, will sometimes last for a long time after exposure, but in a great number of instances are instantly released upon heating the gem.[10]   These color changes may be brought about by the change in the size of particles, the heat readjusting them to their normal condition.

It is claimed that there is no blue pigment in the feathers of birds.[11] The non-iridescent blues, such as the blue of the kingfisher, the blue jay and the bluebird are the same type of structural color.   The only pigment in the blue feathers of these birds is a dark brown one, which apparently serves merely as a background.   The best explanation of these blue feathers is that the horny matter is filled with an enormous number of minute air bubbles which scatter blue light and transmit red.

COLOR OF DISPERSOIDS

In order to explain some of the color changes which take place in dispersion, such as in colloidal gold, emulsions, etc, it is necessary to touch briefly on some of the questions of colors in solutions.   For instance, many solutions in water are colorless, while others are colored. This difference is readily understood when one considers that light is a series of vibrations of different wave-lengths passing through the hypothetical ether.   When all the vibrations pass through a solution, it is colorless, while when all these vibrations are cut off or stopped, the solution is black or opaque.   When some of the vibrations are cut off and others allowed to pass the solution is colored, the color, of course, depending upon the particular wave-lengths of the vibrations that are

[8] Bancroft, *op. cit*, p 251.
[9] Carey Lea, *Am. J. Sci* (3), **33**, 349 (1887)
[10] Newbery and Lupton, *Mem Manchester Phil. Soc.*, **62**, No. 10 (1918).
[11] Bancroft, *op. cit.*, p. 250.

transmitted. This is well illustrated in the case of an emulsion. Quite frequently when an emulsion is properly made it will appear absolutely white, and the more finely the oil globules are dispersed, the more this shades off towards the white, regardless of the color of the oil originally. Many oils which are absolutely black can, by proper dispersion, be made into emulsions which appear as white as milk. In such instances the oil globules are split to a point where they do not permit the vibrations of light to quite pass through; they are all refracted and the product has the appearance of being white, none of the light vibrations being adsorbed In other words, it is the throwing off of the complete spectrum. Naturally, the more finely the product is divided, the more this will occur, until a point is reached where the oil globules are smaller than the period of light vibrations or light waves, the product would then become transparent.

The visibility of particles depends on the difference in refractive index, that is, the difference in refraction of the particles and the medium in which they are dispersed. Therefore, the more hydrous the dispersed phase, the less readily it will be seen.

The color effect of colloidal gold solutions, such as Purple of Cassius, is evidently produced entirely through the absorption of certain light vibrations and the reflection of others, and is probably due to the size of the particles in colloidal dispersion in relation to the light waves. When viewed from this angle, one can readily appreciate the startling color effects that may be obtained in emulsions. By getting the proper adjustment of the refractive index it is possible to get the rainbow effect Also, if a product is dispersed in a medium having the same refractive index as itself, a transparent emulsion is produced.

Chapter IV.

The Relation of Viscosity and Plasticity to the Colloidal State.

The viscosity of a liquid is the measure of its fluidity and is th resistance offered to shearing, stirring, or to the flow through capillar tubes. For example, the viscosity of ether is far lower than that o water, which is again far lower than the viscosity of oils. The detei mination of viscosity is a very important procedure in the industria application of liquids, and is of particular importance in the testing c lubricating oils. (For method of determining viscosity, see Chap ter XV.)

Viscosity is probably best defined as that force which will move unit area of plane surface with unit speed in relation to another parall plane surface from which it is separated by a layer of liquid of a un thickness. A briefer definition of viscosity is the constant ratio c shearing stress to the rate of shear.

The theory regarding the viscosity of emulsions, from a quantitativ point of view, is far from satisfactory, as very little work has bee done in this direction. Dilute emulsions show a viscosity not muc greater than that of water, but the viscosity increases rapidly as tl dispersed phase becomes more concentrated There is a third facto however, which enters into the problem, and that is the emulsifyir agent, which is usually a colloid. It will perhaps make the matter little easier to comprehend if it is pointed out that there are apparent two kinds of viscosity. The first is the one commonly found in sol tions of all crystalloids and some of the colloids. The second is th which is due to the swelling of sub-microscopic solid particles and dependent upon colloidal behavior. The latter type is specific f· colloidal phenomena and depends to a great extent upon the Donna equilibrium [1] This colloidal type of viscosity is of a far greater ma nitude than the usual viscosity brought about in crystalloidal solutior It is this type in which we are specially interested from a colloic viewpoint.

The viscosity of concentrated emulsions is intimately connect

[1] Loeb, "Proteins and the Theory of Colloidal Behavior," 2nd ed, McGra Hill Book Co, New York, 1924, p 259.

with the presence of adsorbed films around the dispersed globules. Especially noticeable in homogenized emulsions is the increased dispersion of the internal phase, whereby the presence of the adsorbed emulsifying agent at the greatly magnified interface confers a marked increase of viscosity to the system.

Deeley and Parr[2] pointed out that in soft solids or plastic substances the so-called viscosity is not constant for all rates of shear, whereas the true viscosity of a liquid is constant.

The word plastic, or plasticity, is frequently used in discussing colloidal substances and the colloidal state. For instance, clay workers use this term in a special sense when they say that the clay is plastic. From the viewpoint of the clay-maker sand would not be plastic, for it will fall to pieces when it is dried. Clay, in presence of water, has some bonding material, usually in a gelatinous form, and the film of water about clay particles is assumed to be about 50 $\mu\mu$ in thickness.[3] If we have this gelatinous film which is adsorbed strongly by the solid particles so as to take up the surplus water, we have this plastic condition. In other words, the clay contains gels and in the presence of water these properties manifest themselves.

As the apparent viscosity of emulsoids varies with the rate of shear, there can be no doubt but that they are plastic when of high concentration or if allowed to age. Garret[4] measured the apparent viscosity of gelatin by two methods, in which the rates of shear were different (failed to agree), thus indicating that the gelatin solution was plastic.

Since colloids do not have definite melting points, boiling points or solubilities, it is most unfortunate that the outstanding property of colloids, their viscosity, is merely a relative quantity and not a fundamental physical constant independent of the instrument in which the viscosity is measured. The viscosity of colloids frequently proves to be a false guide and it would be very unsafe to make any broad statement in defining a colloid by its viscosity. If the viscosity could be shown not to be a fundamental property, then the lack of its control would not be so important.

The properties of plasticity, hardness, malleability and ductility, when applied to soft solids or colloids, are complex and cannot be properly represented by a definite quantity, but it is most important that they be measured with precision in terms of yield value and mobility. It would be advisable, if one would keep in mind the difference between apparent viscosity and true viscosity, that the material be considered plastic when the ratio of shearing stress to the rate of shear

[2] Deeley and Parr, *Phil. Mag.*, **26**, 87 (1913).
[3] Bancroft, "Applied Colloid Chemistry," 2nd ed, McGraw-Hill Book Co., New York, **1926**, p. 191
[4] Garrett, *Phil. Mag*, **6**, 374 (1903).

varies, and that the material be considered viscous only when the ratio is found to be constant

The ratio of shearing stress to the rate of shear, at a given temperature and pressure, remains constant for true liquids, and does not vary much in homogeneous materials. Where there is a variation in the apparent viscosity in tests of other materials, this should be taken as an indication that the material is plastic The consistency of plastic materials should be expressed by an equation which defines the variable between the rate of flow and the force which produces it.

The viscosity of colloids may increase enormously with the concentration. With a 1 per cent solution of agar, which would form a solid gel, it is, undoubtedly, largely a question of structure, similar to a concentrated emulsion where it may reach the point to take on a certain gel formation We might have, for instance, minute globules of oil coated with a viscous soap film, which may be set into a sort of honeycomb or gel structure. These are of vital importance in their relation to so-called colloidal viscosity.

Viscosity is obtained in true solutions as well as in mixtures of liquids, but when a powder or other finely divided material is added they will become plastic if of sufficiently high concentration. Thus, paints and pigments in the true sense are probably plastic materials, as they do not conform to the requirements for a truly viscous liquid. One plastic material may have a high yield value and high mobility, while another may have a lower yield value and also lower mobility. They might still show the same apparent viscosity but they would not have the same consistency. This differentiation has caused considerable confusion among colloid chemists and the problem is one of frequent debate. However, the slightest pressure will produce flow with viscous materials, regardless of one's viewpoint on the matter. This flow, of course, may be slow with very viscous materials. With plastic substances the flow is proportional to the pressure in excess of a certain minimum yield value which is required to start the flow.[5] Beyond this point the flow increases proportionally as the pressure is increased. When one studies the fluidity concentration curves of a colloidal solution, one is impressed with the fact that the fluidity, as ordinarily measured, reaches a zero value at a definite concentration and then takes up what may be classified as plastic flow.

There is a very fine dividing line in some cases between a viscous and a plastic material. A plastic material is usually classified as some substance which requires a pressure to make it flow, while a viscous material does not require pressure In a plastic material, a permanent deformation does not involve a rupture. For instance, there are a

[5] Holmes, "Laboratory Manual of Colloid Chemistry," Wiley & Co, New York, 1922, p. 67.

lot of heavy pastes that are plastic, while a heavy oil is viscous. A plastic substance can be molded by pressure, hence, any break in it is self-healing, while a liquid cannot be classified as plastic, for it will not retain its shape; but if we increase the viscosity of a liquid it finally reaches a point where it becomes plastic Bancroft[6] gives some very good illustrations of this, from which the following is quoted: "Molasses candy is plastic until it crystallizes; semi-fused glass is plastic; sealing wax is brittle if the pressure is applied rapidly, but is plastic if the rate of deformation is slow Since metals and other solids coalesce under high pressure, there is no reason why they should not be plastic under the same conditions, as indeed they are. We make use of this property when squirting metals into rods or pipes." Ice is also plastic under high pressure.

"Between the extreme cases of a solid, such as metal, and a liquid, such as glass, we have the intermediate state such as putty, which is whiting mixed with oil, or a solid with a liquid film around it. If a liquid is adsorbed by a solid, thin films of the liquid will hold the solid particles together while still permitting them to move relative to each other. This tendency of liquid surfaces to coalesce will cause any break to heal. A liquid film may, therefore, act as a bond for solids and make the mass plastic."

The elasticity of materials may be due to a combination of elastic and viscous properties, but there is no general agreement as to the best methods of measuring these. The elastic effects frequently occur with soft or plastic solids. If the stress is light enough and not prolonged, a solution containing only 5 grams of gelatin per liter is elastic, while glycerin and sugar solutions show only the viscous phenomena.[7] According to Schwedoff, the higher the elastic limit, the more perceptible is the variation in viscosity, and viscosity is not constant except for liquids which show no trace of elasticity in shear. He is speaking, however, of apparent viscosity and it must be constantly remembered, in reading works on colloidal chemistry, that the distinctions between viscous and plastic materials are not generally recognized. This matter has frequently been discussed over a period of the last fifty years or more.

[6] Bancroft, *op cit*, p 186.
[7] Schwedoff, *Congress Int. Physique,* 1, 478 (1900)

Chapter V.

Adsorption.

Every solid surface has an attraction for other substances, which varies to a great degree with the material or substance involved   This holding to a surface is called adsorption as differentiated from chemical reactions of solid solution   Some solids have far greater adsorbing power than others, and a given adsorbent shows preferential adsorption. It is common knowledge that such substances as charcoal and various colloidal filter mediums have power to take up various gases in large quantities; also that such materials can adsorb various constituents from solutions.   Advantage has been taken of the adsorbing property of carbon in the purification of sugar, whereby the coloring matter is removed from the sugar syrup and a clear colorless solution obtained. Many substances in a fine state of division, which have large contact surfaces exposed, have a similar property.   Plants adsorb food from soils by the principles of adsorption, and the substance taken up is first bound to the surface of the adsorbent   It is believed the adsorbed substance is not in chemical combination.

We come very much in contact with the principles of adsorption in the case of dyes, and a large number of precipitates adsorb ions from solution.   Another common daily occurrence of adsorption is that of glues, which adhere to the solid matter and are powerfully adsorbed, giving a firm bonding surface   "Adsorption may be considered a concentration of dissolved or dispersed substances upon the solid, liquid or gaseous adsorbing surface.   After concentrating there, the adsorbed substance may react or polymerize, or dissolve, or it may be coagulated or crystallized out slowly " [1]   Therefore, the whole theory of adhesives depends, to a great extent, on the cementing of the materials by some product which is strongly adsorbed by each surface, and agglomerates or hardens so as to bind the two surfaces together.

There is no doubt that adsorption plays a prominent rôle in colloidal dispersion   When colloids are precipitated by electrolytes some of the ions, as a rule, are carried down with the precipitate and adhere so firmly that they cannot be removed by washing.   This is entirely a matter of adsorption   With colloidal particles, or those in a fine state

[1] Holmes, "Laboratory Manual of Colloid Chemistry," Wiley & Co, New York, 1922, p. 68

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of dispersion, which have such large surfaces in contact with the substance in which they are dispersed, it is quite obvious that the phenomenon is entirely that of surface adsorption. Peptization is also brought about through adsorption of certain ions Albumin is a typical example, for when it carries a negative charge in an alkaline solution, a strongly adsorbed anion will make it more negative and by increasing the potential difference will make the dispersion more stable. It will be harder to precipitate with sodium salts after the adsorption of the anion under such conditions. In acid solutions, however, the sodium salt with the more strongly adsorbed anion will be more effective in causing precipitation Under such conditions we are neutralizing the positive charges on the micelle and thereby bringing about flocculation through the adsorption of the anion. This means that in dispersions of this sort, if the ion with the opposite charge is present, it neutralizes the charge on the dispersed particle and flocculation results.

When a dispersion is stabilized by an adsorbed ion of similar charge, coagulation depends upon the washing out of such ion in order to avoid reversing, and the more strongly the precipitate is adsorbed, the more difficulty there will be in washing it out. For this reason, when albumin is precipitated by sodium chloride, the coagulation is usually reversible, while when precipitated with a salt of the heavy metals, it is not so readily reversed. Similar action has been pointed out by Linder and Picton [2] in quantitative analysis. They found that barium precipitated arsenic sulfide in a manner so that it could not be readily washed out In this instance a bivalent salt was used, but by treating the precipitate with an excess of ions which are more powerfully adsorbed, such as NH_4^+, the Ba^{++} was replaced by the equivalent amount of NH_4^+.

Aniline dyes, while insoluble in benzene, can be peptized by a benzene-soluble colloid, such as zinc or magnesium resinates. Similar results can be obtained with most of the bi- and tri-valent soaps. Adsorption will cause peptization under the right conditions, but the disintegrating power of the adsorbed substance may be fairly small. In such instances the adsorbed substance will not be sufficient to break up the solid masses so that peptization takes place, but a protective colloid may prevent the formation of a precipitate, although it has not sufficient power to disintegrate such a precipitate after it is formed Therefore by dispersion with a colloid mill peptization may take place with small amounts of peptizing agents.

Bancroft [3] has pointed out that sodium chloride crystallizes under

[2] Linder and Picton, *J. Chem. Soc.*, **67**, 63 (1895).
[3] Bancroft, "Applied Colloid Chemistry," 2nd ed., McGraw-Hill Book Co, New York, **1926,** p. 198

different conditions in acid or alkaline solutions. If crystallized in an acid solution there is presumably strong adsorption of the hydrogen ion, and in an alkaline solution there is strong adsorption of the hydroxyl ion. The addition of alcohol cuts down the adsorption of negative ions, and should counter-balance the effect of the alkali, thus causing the sodium chloride to crystallize in cubes as it would in a neutral or acid solution. Such was found to be the case. This shows the effect of eliminating the adsorption of the hydroxyl ion in an alkaline solution.

THE WETTING OF SOLID PARTICLES

Adsorption is an important factor in the wetting of some solids by liquids. If the solid particles are finely divided, they usually have a cushion of air about them, and when the fine powder is put into the liquid, the particles are airbound. That is, the little particles carry the air in with the powder, due to adsorption. This air may afterwards be displaced very slowly and this brings in the time factor. While we do not know what factors determine the amount of water adsorbed on fine crystals, there is no doubt but that different degrees of adsorption take place with various substances, hence the wetting power is entirely different. Some substances are easily wetted while others are resistant to wetting and, in a great number of instances, due to the affinity they have for adsorbing air upon the surface of the particle, the particles do not come in contact after the powder is agitated in the presence of such liquid. An excellent example of this is in the case of very finely divided calcium carbonate. If this is added to water and agitated, one may obtain a thick paste after the addition of about 25 per cent of carbonate. If this material is then passed through a so-called colloid mill, it is possible to shear off the air cushions and get a proper contact angle of the water with the powder. This dispersion, upon discharge from the colloid mill, will be found to be very fluid again, due entirely to the elimination of the air cushions. An additional 25 per cent of calcium carbonate can then be added to the dispersion and the operation repeated. A material will be obtained which is at least 50 per cent calcium carbonate and yet very fluid. This demonstrates that the original pasty condition was caused by the adsorption of air on the fine particles. Once this was eliminated and the liquid brought in true contact with the surfaces the dispersion was again quite fluid. Similar experiences are encountered with a great number of substances in a finely divided state   With the usual methods of mixing it is impossible to release the air cushions from the finely ground particles, but through proper mechanical treatment these may be removed and a large amount of such substance incorporated into

the liquid medium   This is all due to the adsorption and the elimination of air from the surfaces of the finely ground solid material. Once it is wetted with the vehicle it will remain in a finely divided condition, provided there is not present an ion of opposite charge or some other condition of this sort to cause flocculation.

It is not easy to peptize gum arabic by agitation in water because the water does not displace the air from the gum. If this ground gum is added to oil, alcohol, etc., so that it may be maintained in a finely divided state, then when the water comes in contact it meets with the individual particles   These particles, of course, are not peptized by oil, alcohol and such materials. The air is readily displaced in the presence of liquids in which the gum is not soluble   When it comes in contact with the water, it is possible to get instant wetting and thus rapid peptization in the water phase   Advantage has been taken of this in the manufacture of various emulsions wherein the finely ground gum arabic is added to the oil phase, then the water allowed to come in contact with violent agitation. This eliminates, to a great extent, the so-called balling action of the particles which are air-bound. By proceeding as above described, manufacturers have been able to work commercially with such gums, making emulsification direct with no appreciable period of time necessary for allowing the gum to be peptized by the water   This process is described more fully in the chapter on emulsification (*see* p. 120).

Bancroft[4] points out a number of very interesting illustrations of the extent of air adsorption on the surface of solids   Among these is the fact that a tent will not leak in a heavy rain until someone touches some point on the canvas. This contracts or expands the air spaces, and when the fingers are removed from this contact point, the air has been driven out of the canvas   The tent will leak until it has been dried out and air has been allowed to get on to the surface of the fabric through adsorption; or, as stated, "If the air spaces contract, air is driven out, and when the fingers are taken away water enters. If the air space expands, water runs in. In either case the air is displaced at the point of contact and the water enters and the tent continues to leak once the air is displaced." Also, take the case of water wings, which are made of a fine-meshed fabric. After they have once been wetted, so that a film of water is formed in the pores, the strength of the film is sufficient for the wings to be blown up without the air escaping.

The Effect of Valence on Adsorption

In the production of stable dispersions, the whole of the forces of each atom of the compound are supposedly completely satisfied, but

[4] Bancroft, *op cit ,* p. 80.

the theory of valency, especially under recent investigations, goes to indicate that polar forces or residual valences exist. Such forces may be residual and similar to those acting between two oppositely electrically charged bodies. This matter of secondary valency, to be properly understood, would require more knowledge regarding the electrons. All of these are factors in connection with adsorption. Charcoal, for instance, adsorbs both acid and basic dyes. Alumina takes up many acid dyes but not the basic. Silica, tannin, etc., have a high degree of adsorption towards basic dyes. Wool adsorbs relatively few. Advantage is taken of this fact in dyeing rayon when in combination with silk. The silk adsorbs certain dyes that the rayon will not adsorb. In this way various blends of color effects are accomplished by the dye, silk taking one color and the rayon taking another.

As a general rule, it is safe to state that the ion of higher valency will be adsorbed more strongly than that of lower valency,[5] and this is true in most instances. However, if the substance were dissolved in a solvent, where the affinity of this solvent for the product is very great, the degree of adsorption would not be so much. For instance. an aqueous solution of methyl violet may be decolorized by the use of charcoal. This substance, however, may be very soluble in alcohol, which would remove the color from the charcoal. Hence, the solvent is most important in considering any rule on degree of adsorption.

The Effect of Temperature

Another factor which is most important in adsorption is that of temperature. For instance, wool takes up very little acid dye at ordinary temperatures, but if this is increased the degree of adsorption increases enormously and this adsorption is not reversible. The acid dye which was adsorbed at a higher temperature cannot be washed out at low temperature as a general rule.[6] This is probably due to the fact that the dye after being adsorbed agglomerates and will not be taken up again by the water, or is practically insoluble. This wool can then be submerged again in an acid dye, and perhaps take up more coloring matter, due to the increase in adsorption at higher temperatures.

Adsorption of Ions

It is common practice to peptize precipitates by adsorption of the ion of an electrolyte on the surface of the particles of such precipitates. By this adsorption the precipitate is peptized, all particles taking

[5] Schulze, *J. prakt. Chem.*, **25**, 431 (1882), **27**, 320 (1883)
[6] Lake, *J. Phys. Chem.*, **20**, 761 (1916).

on the same charge and thereby repelling each other and promoting stability in the suspension   Clays may be kept in suspension in the water phase for a longer period of time by this means. In fact, in all mechanical dispersions, preferential adsorption of either the hydroxyl or hydrogen ions is to a large extent the secret of maintaining stability.   To have stability the particles must all carry like charges so as to repel each other, and this is a very important point, as has been pointed out. This invariably leads directly back to the importance of maintaining a proper hydrogen-ion concentration. If the conditions are not right, no matter how fine the dispersion may have been, it will flocculate and the work is entirely undone. This means that the obtaining of the proper adsorption of ions on the surface of the substance dispersed, and under the right conditions, is most essential.   This is nothing but preferential adsorption (*see* Selective Adsorption, p. 49).

Lachs and Michaelis [7] state that an anion is more readily adsorbed in the presence of an adsorbed cation. On the other hand, a cation is more easily adsorbed in the presence of a readily adsorbed anion   In dyeing fabrics an acid dye will be taken up more readily in an acid solution than in one which is neutral or alkaline, for the reason that a readily adsorbed anion will decrease the amount of dye taken up, while a readily adsorbed cation will increase it.[8] The same applies in the case of basic dyes, because the color is in the basic radical It will therefore be taken up more readily in a basic solution; and, if a given substance adsorbs a base more readily than an acid, there will be a tendency for the salt of that base and that acid to hydrolyze, the base then being adsorbed to a greater extent than the acid

It is common knowledge that the hydrogen and hydroxyl ions are in a class by themselves, and are different from other univalent ions, for they are in most cases adsorbed much more strongly. These ions, however, are present—to any extent—only in electrolytes which have a great deal of dissociation, such as caustic soda and hydrochloric acid. We cannot, of course, have a high concentration of both hydrogen and hydroxyl ions at the same time as this would be entirely contrary to the law of mass action. In hydrolysis, if the caustic soda could be removed by adsorption, such hydrolysis could proceed and would be dependent upon the degree of adsorption of the base. Of course there is always hydrolysis but this does not, as a rule, proceed very far for the reasons given above. By employing the principles of adsorption, however, we frequently can take advantage of such hydrolysis where it is desirable to have it proceed in the manufacture of some definite product

[7] Michaelis, *Z Electrochem*, 17, 1 (1911).
[8] Bancroft, *op. cit.*, p. 133.

OTHER TYPES OF ADSORPTION

While the discussion above has been principally upon the question of adsorption upon the surface of solids, there are also various other types of adsorption. For instance, the equilibrium between a liquid and its vapor is believed to have no abrupt transition point from the liquid to the vapor phase. Over a narrow range all of the various densities intermediate between the vapor and the liquid phase actually occur, so that we have liquid adsorbing its own vapor. A gas or vapor may be adsorbed on the surface of a solid. This is now being commercialized to a great extent. One of the recent applications involving this principle is a new type of refrigeration, wherein silica gel is used to adsorb a vapor. This is then heated and driven off in concentrated form, liquefied and used for recirculation for cooling.

When a liquid is adsorbed upon the surface of a solid, forming a liquid film, it is commonly stated that the liquid wets the solid. If it were not for the adsorption of this liquid upon the solid surface, however, the solid would not be wetted. This is sometimes explained by the statement that the contact angle is not correct. For instance, water will wet the surface of glass, while mercury does not. Hence, a column of mercury rises in the center of the meniscus, while with water the meniscus is concave. Therefore, there is a contact angle when the liquid wets the glass. For a liquid to wet a solid substance in the presence of air, it must be more strongly adsorbed so as to displace the air. Otherwise, this condition must be brought about through proper mechanical dispersion, which will speed up the degree of adsorption of the liquid and displace the air. This may be brought about through heating in a great number of instances. The floating of metal powders, or actually the floating of pieces of metal, upon water is on account of the slowness with which water is adsorbed. Hence, there is an air cushion which must be replaced by the water before the metallic particles will sink.

SELECTIVE ADSORPTION

Selective adsorption is an important factor when one is adding powders to liquids, and this has some important commercial applications, especially in the paint industry. In mixing paints, where the pigments are added to the vehicle, prolonged mixing is sometimes required before the pigment has been thoroughly wetted by the vehicle. In such instances, the colloid mill has had numerous commercial applications. It gives a fine dispersion through deflocculating the particles and bringing them into intimate contact with the vehicle. The air is displaced and the final product is what is known as a smooth-mixed paint or pigment. This is sometimes spoken of as fine grinding. As

a matter of fact, the colloid mill does not grind. It merely deflocculates the groups of particles, bringing the proper contact of the vehicle with pigment and causing instant wetting down One can readily appreciate that adsorption is a big factor here and that by the use of the colloid mill the adsorption of the vehicle on the surface of the pigment has merely been speeded up This, of course, is a tremendous commercial advantage and means large output of mixed paint

Any treatments which cut down the amount of adsorbed air on the surface of fine powders will, of course, result in their being more easily wetted, thus, it is a matter of selective adsorption. When one liquid is adsorbed more readily than another, the first will displace the second from contact with the solid; hence, the reason for greasing pans, such as in the frying of eggs, etc. Air adsorption is the success of aluminum griddles. The reason they do not require greasing is that the air forms a film which keeps the cakes from sticking to the pan.

A solid which is wetted by a liquid adheres to the liquid. This is the basic principle of the modern so-called colloid mill; especially with the smooth-surface type. The liquid adheres to two surfaces, one of which is rotating at high speed This gives a lamination, or shearing action, brought about in a film type of colloid mill. Again, it is entirely a matter of adsorption, otherwise the film colloid mill would be a failure. A portion of the film adheres to one part of the machine and another portion of the liquid to another part which is rotating at high speed This results in the laminating and shearing action of the machine.

Cotton will adsorb some of the base from sodium chloride when in solution and leave the solution slightly acid. This effect may be masked to some extent if a colloidal substance is present, such as a gelatin, casein, etc. Of course, in the presence of any quantity of sodium chloride solution, the protein would be precipitated, but slight traces would effect this reaction. Such demonstrations impress one with the importance of adsorption In commercial operation, in a great number of cases, where a variation in chemical activity is obtained adsorption is the entire cause Unfortunately, in such instances it is very frequently overlooked. The hydrogen-ion concentration in such mixtures should, therefore, be closely watched in order to determine whether adsorption is interfering seriously with the production.

Effect of Adsorption on Coarse and Fine Powders

It has been pointed out by Fink [10] and also by Briggs [11] that fine powders adhere to coarser particles when they are mixed together. To

[10] Fink, *J Phys Chem*, 21, 32 (1917).
[11] Briggs *J. Phys Chem.*, 22, 216 (1918).

illustrate, when a coarse red powder is mixed with a fine white powder it will appear white; but, if in the mixing the red powder happened to be fine and the white powder coarse, the appearance of the mix would be red. There are a great number of red paints used each year which contain as high as 90 per cent of natural barytes; the white material does not show up, however, because of the fineness of the red powder. This fact is taken advantage of to obtain cheap fillers in commercial products. This behavior of powders is of considerable importance when mixing inert fillers in paints. The finer powder is adsorbed on the surface of the coarser; and, instead of filling the voids in the space occupied by the coarse powder, the fine powder is adsorbed on the surface. The color of the coarser powder may be masked completely by a comparatively small quantity of fine powder, if it is fine enough to have proper covering power.

The adsorption of the finer material on the coarser can also be used to advantage in electrical insulation. Fink has shown that a white non-conducting powder like thoria, with a black conducting powder like tungsten, may be either black and an electrical conductor, or white and a non-conductor, depending entirely upon the relative coarseness of the two powders; the finer in each case determines the insulating properties

The adsorption of the finer powder has some other interesting applications in its effect on taste. This is well illustrated by an example, cited by Bancroft,[12] showing the effect of change in flavor when the finer material is adsorbed on the coarser. When paprika and sugar are mixed, if the sugar is very fine and the paprika relatively coarse, the first taste of this mixture will be sweet When the sugar is coarse and the paprika very fine, the mixture will not have the sweet taste The finer powder in each case has coated the coarser and determines the taste. This fact is taken advantage of in the coating of pills.

This phenomenon also explains some very peculiar results frequently encountered in the manufacture of various preparations. For example, in a phosphate baking powder the monocalcium phosphate is protected from moisture by a mixture of fine starch The calcium phosphate must not be too fine; the starch, on the other hand, must not be too coarse, so as not to be adsorbed. It is claimed that potato starch cannot be substituted for corn starch in the preparation of such baking powders due to its difference in degree of adsorption.

ADSORPTION OF GASES

In order to form a mental picture of what takes place when a gas is adsorbed on the surface of a solid, one must conceive that the atoms

[12] Bancroft, *op cit.*, p 94.

on the outer surface of the solid are in a different state from those in the interior of the mass. They do not have similar atoms in contact with them on the outer surface. In other words, it is believed that the atoms on the outer surface of a solid are oriented and that there exist forces of attraction on the outside of a solid which cause adsorption and that these forces hold the mass together throughout the solid. That is to say, there is a residual valency, as previously explained, and adsorption is due to the saturation of these valences.

While it is not believed that adsorption is a chemical reaction such as we usually picture it, in some cases of adsorption compounds are formed. For instance, it is believed that when platinum black adsorbs oxygen some of this gas is taken up and is present as the oxide in combination with the platinum. While the adsorbed substance is chemically united with the adsorbing material, it is merely satisfying the residual valency, and it varies in proportions. As an illustration, Langmuir [18] points out the adsorption of chlorine gas by charcoal; the whole of the charcoal and the whole of the chlorine are considered as forming a compound. The composition varies continuously as the chlorine is pumped out, and does not obey the laws of Dalton. If one desires to regard adsorption as a chemical reaction one must consider such cases as indefinite compounds and to differentiate them from what is commonly conceived as a chemical compound.

Adsorption is an important factor in the use of catalyzers and in work on contact catalysis. In such instances, the reaction velocity can be increased in two ways, either by increasing the chemical potential or by decreasing the chemical resistance, for the reasons above given. Increased concentration, due to adsorption at the surface of a solid, will, of course, increase the reaction velocity, regardless of any catalytic agent which may be present.

ADSORPTION IN FILTRATION

In all cases of ultra-filtration care must be taken that filtration is really taking place and that the results are not due somewhat to adsorption. As an illustration, if chromic oxide is peptized by alkali, a deep green solution is obtained, but when passed through an ultra-filter, the filtrate is colorless. If such solution, however, stands for a sufficient period of time, the chromic oxide in dispersion becomes sufficiently coarse so that it can be separated even by means of an ordinary filter. The action of the ultra-filters is due to the size of the pores in relation to the size of the particles. If two substances are present which do not adsorb each other, and these are of different particle size, separation may be accomplished by the use of ultra-filters.

[18] Langmuir. *J. Am. Chem. Soc.*, **39**, 1848 (1917).

An ultra-filter will retain the Prussian blue from a mixture of Prussian blue and hemoglobin and the filtrate will be red. If the Prussian blue is mixed with arsenic sulfide, adsorption takes place and the entire product is blocked on the filter. Either one of the ingredients might be sufficiently fine to pass through alone, but after such adsorption, the entire product has been blocked by the pores of the filter [14]

If a substance does not pass through the ultra-filter it is perfectly true that this substance is not in solution; it is merely in a state of dispersion However, the fact that it does pass through is not positive proof that the substance is not dispersed in the liquid, for the pores of the ultra-filter may be larger than the dispersed particles. There is no doubt, however, that anything stopped by the ultra-filter is in suspension. The ultra-filter is a porous membrane and should be looked upon more as a fine sieve If arranged sufficiently fine, it will, of course, block very fine particles due to the small size of the openings. If there is another product present which is adsorbed in the mixture, the entire dispersed product may be blocked.

There is a fundamental difference between a semi-permeable membrane and an ultra-filter. A semi-permeable membrane is a continuous film, and has a marked negative adsorption. If it is porous, the pores are so small that all liquid in the pores is adsorbed. A semi-permeable membrane will allow the ions to pass through and also materials in a molecular state in solution, but will block colloidal dispersions Some of the colloids may be reduced to a very fine degree of dispersion, such as the gelatin micelle, and yet be blocked by such semi-permeable membranes. The original division between matter in the so-called colloidal solution and that in crystalloidal solution was determined by a dialyzer or membrane of this type.

It will readily be appreciated from what has been said that adsorption enters into most problems of mechanochemistry, and is a factor that must be constantly kept in mind when dealing with fine dispersions.

[14] Bancroft, *op. cit*, p. 220.

Chapter VI.

Electrical Concepts and Their Importance in Colloidal Dispersion.

DISSOCIATION

The distinguishing feature between what are known as electrolytes and non-electrolytes is presence or absence of an electrical charge when in solution—whether, when in the presence of water or other dissociating solvents, they break down into charged parts or ions, or whether they are not thus dissociated but remain in solution in the so-called molecular condition. As an illustration, we might take sodium chloride or common salt, which when dissolved breaks down into the ionic condition, the sodium taking on the positive charge and the chlorine the negative charge, and sugar, which dissolves in the molecular condition and does not dissociate, but remains in the molecular condition and is uncharged For the benefit of those who have not had occasion in recent years to study chemistry from the modern viewpoint, we shall deal briefly with the subject of dissociation so they may obtain a clear picture of the question of electrical charges on colloidal particles.

In true solutions ions are formed from molecules in a number of different ways, but most frequently by the molecules breaking down into their equivalent number of cations and anions, the cations being the positive charges which migrate to the cathode or negative pole, and the anions being the negative charges which migrate to the anode or positive pole, when an electrical current is passed through the solution. In other words, ions are produced when acids, bases and salts are dissolved in water or other dissociating solvents and pass into what we call true solution Nitric acid in the presence of water is dissociated into hydrogen ions and nitrate (NO_8) anions, and all other acids are dissociated into hydrogen ions and anions of a nature depending upon the acid in question. Thus, an acid may be defined as any compound which in the presence of a dissociating solvent yields hydrogen ions.

A pure homogeneous substance is not dissociated at ordinary temperatures, therefore could not under ordinary conditions be an acid A demonstration which is commonly referred to, to illustrate this point,

is that pure hydrochloric acid gas, or even liquid hydrogen chloride, will not decompose carbonates, which, of course, it would do in the least presence of water or other dissociating medium   Furthermore, if the hydrochloric acid-gas is dissolved in a solvent in which it does not dissociate, for instance, chloroform or benzene, it will not decompose carbonates nor will it show any acid indications with test papers or indicators.[1]   Therefore, to have the effect of an acid, we must have hydrogen ions present in a dissociated form

A base neutralizes an acid to form a salt, and when dissolved in water will dissociate into hydroxyl anions, while the cation will consist of the metal of which the base is composed.   For instance, sodium hydroxide dissociates into hydroxyl anion and sodium cation   All bases, therefore, yield hydroxyl ion as the anion.

The most important classes of crystalloid chemical compounds are acids, bases and salts, which taken as a group, constitute what is known as electrolytes.   All of these compounds when dissolved in water or other dissociating solvents are broken down in varying degrees into their ionic condition, that is, they are electrically dissociated.   The conductivity of the solution depends upon the ions present and their velocity of travel, for these particles, of course, carry the charges.

HYDROLYSIS

The only action of water on salts and other electrolytes thus far discussed has been electrolytic dissociation, in which the molecules of the electrolyte are broken down into the positive and negative charges There is a different kind of dissociation of salts effected by water known as hydrolytic dissociation, which is fundamentally different from electrolytic dissociation, although the products of hydrolytic dissociation are generally electrically dissociated also   This is sometimes spoken of as "hydrolysis," and is the reason why solutions of some supposedly neutral salts have acid reactions and others alkaline or basic

Aluminum chloride might be a good salt to use to demonstrate a typical case of hydrolysis.   It is acted upon by water to a slight extent:

$$2AlCl_3 + 6H_2O \rightleftarrows 6HCl + 2Al(OH)_3$$
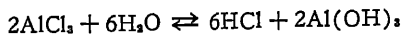
As aluminum hydroxide is a weak base, it is only slightly dissociated, and therefore yields very few hydroxyl ions   Hydrochloric acid, on the other hand, is classified as a strong acid, by which is meant that it is strongly dissociated into its ions   The hydrogen ions are in excess of the hydroxyl ions and the solution gives an acid reaction, as indicated by the above equation

Hydrolysis is a general phenomenon and salts in general are hydro-

[1] Jones, "The Nature of Solution," D. Van Nostrand Co, New York, 1917, p 136.

lytically dissociated by water. Salts formed by combination of strong acids with strong bases undergo only slight hydrolysis Salts of weak acids combined with weak bases are strongly hydrolyzed, while salts of weak acids with strong bases (and *vice versa*) are hydrolyzed to some extent, but the magnitude of the hydrolysis depends upon the strength of the acid and the base which forms the salt in question By strength is meant the dissociating power. Water will hydrolyze any salt until the product of the concentration of hydroxyl and hydrogen ions reaches a certain value. If either the base or acid of the salt is only slightly soluble, the hydrolysis will go further than if both are strong electrolytes.[2] A stage of equilibrium is finally reached, this stage can be reached more rapidly by heating, which accelerates the chemical activity.

Although hydrochloric acid is classified as a strong acid, its salts formed through combination with weak bases, such as aluminum chloride, are hydrolyzed by water, especially at the more elevated temperatures, and the resulting hydroxides are in a state of colloidal dispersion.

Dissociating Power of Solvents and Their Dielectric Constants

Thomson [3] was the first to point out the important relations between the dissociating power of solvents and their dielectric constants Nernst [4] closely followed this with an independent investigation. Because of its importance in colloidal dispersions, it is deemed advisable at this point to explain just what is meant by the dielectric constant of a medium. It is a property similar to what Faraday called "the specific inductive capacity." The numerical value of this constant determines the force of attraction between opposite electrical charges when separated by·the medium in question. It is sometimes defined as the relation between the force exerted between two charged bodies when separated in a vacuum. The law governing such phenomena is that of Coulomb.

If we have two electrical charges designated by I_1 and I_2 separated by a distance r, the forces of repulsion or attraction f between these charged bodies may be expressed by the following equation. K is the dielectric constant of the separating medium between the two charges.

$$f = \frac{I_1 I_2}{r^2} = \frac{1}{K}.$$

From this equation it will be noted that the larger the value of K, which is in the denominator, the smaller the electrostatic force acting

[2] Bancroft, "Applied Colloid Chemistry," 2nd ed, McGraw-Hill Book Co, New York, 1926, p. 208.
[3] Thomson, *Phil. Mag.*, 36, 320 (1893).
[4] Nernst, *Z. phys Chem.*, 13, 53 (1894).

between the charges, or in other words, the force is inversely proportional to K.

The relation between the dielectric constant of the media and their own power to dissociate molecules dissolved in them is explained quite fully by Jones [5] who says: "The author has been best able to form a picture of this relation in the following manner. Take, for example, a solvent like water, which has a large dielectric constant. The force of attraction between the positively charged cation and the negatively charged anion of the electrolyte dissolved in the water is inversely proportional to the dielectric constant of the solvent This being large in the case of water, the force of attraction between the positively and negatively charged parts is small. There being but a small force to hold the cation and the anion together in the molecule, they separate or undergo electrolytic dissociation readily."

The importance of the part played by the dielectric constant, and its effect on variation in electrical charges leading up to the charges on dispersed particles, will be fully appreciated after giving some typical illustrations which show that this factor must not be overlooked in considering the charges upon particles.

When two dry substances are rubbed together so that they become electrically charged, one tends to become charged positively and the other negatively. In other words, one of these substances either adsorbs positive ions or loses negative ions Coehn [6] formulated the rule that the substance with the higher dielectric constant takes the positive charge. Vieweg [7] elaborated upon this by stating that "the dielectric constant of a substance is a measure of the force existing between two different charges on the substance, the force being the less the greater the dielectric constant " In other words, when two non-conductors are brought into contact, it is readily appreciated that the substance with the higher dielectric constant will take on the positive charge, as it has lost an electron and will exert a lower attractive force than will positively charged atoms on the surface of the substance with the lower dielectric constant; that is, the available electron will pass to the substance with the lower dielectric constant, so that when the substances are rubbed together the higher dielectric constant will have a positive charge, according to Coehn's rule

This effective transfer of electrons is dependent upon the nature and structure of the atoms on the surface of each substance. Bancroft [8] has pointed out that "in no case is it possible to obtain any electrical charge from two like faces of a crystal when they are rubbed

[5] Jones, *op cit*, p. 210.
[6] Coehn, *Z. Electrochem*, 16, 586 (1910).
[7] Vieweg, *J. Phys. Chem.*, 30, 777 (1926).
[8] Bancroft, *op. cit*, p. 281.

together", thus arises the method of detecting whether two faces of a crystal are alike Thus, two faces of gypsum parallel to good cleavage might be considered alike, but the 010 and the 0$\overline{1}$0 faces charge each other when the crystal is pulled apart or when the two faces are rubbed together, showing that they are different on the surfaces. Consequently, when considering the properties of atoms in a crystal, it must be remembered that the electrical structure of an atom is modified when it is part of a compound, and that, while if the faces are identical there will not be any charges, when they are rubbed together, if there is the least variation, there will be. In other words, it is all a matter of the structure of the surface. For instance, barium sulfate or barite, $BaSO_4$, charges celestite, $SrSO_4$, negatively and this in turn charges anhydrite, $CaSO_4$, negatively. This shows that the tendency to lose an electron is greatest for barium and least for calcium, which agrees with the fact that calcium more closely approaches the noble metals in the electrochemical series than does barium.

Transfer Effect in Presence of Water and Electrolytes

The important question to consider in the case of dispersion of solids in liquids is what happens when various substances are in the presence of water, or other liquids, in which they would be dispersed by mechanical shearing action It is found that quartz glass, composition insulation, sealing wax, silver, etc., if wetted by means of condensed steam, become positively charged when rubbed together, the negative charge going into the air, and that with less moisture present, intermediate values are obtained. Take the three pairs of substances, serpentine and fur, calcite and cheesecloth, beryl and blotting paper, where the first in each case is normally positive to the second and the second absorbs water more readily. In all of these cases Bancroft[9] points out that it is possible to have these substances come to equilibrium with unsaturated water vapor and then have the second one of the pair charge the first one negatively instead of positively when rubbed together. Also, when their surfaces were moistened with two per cent solution of sodium chloride instead of with condensed water, they both took a negative charge when they were rubbed together, and the positive charge went off into the air. This reversal takes place with sodium chloride between $0.01N$ and $0.1N$, and with hydrochloric acid between $0.0001N$ and $0.001N$, and with sodium hydroxide between $0.1N$ and $1.0N$ Simpson[10] found that drops of pure water become positively charged when split, but the experiment failed when water was taken from the city water

[9] Bancroft, *op cit*, p 282
[10] Simpson, *Phil Trans.*, **209A**, 379 (1909).

supply which evidently contained enough salts to offset the results of the experiment.

Lenard [11] found that drops of water at the bottom of a waterfall are charged positively while the air in the vicinity has a negative charge. This is often referred to as waterfall electricity. The nature of the surrounding gas seemed to have no effect upon the charge, but when salt was added to the water until the concentration exceeded 0.011 per cent sodium chloride, the droplets took on a negative charge and the air a positive one. Hence one realizes the important changes brought about by the addition of a small amount of electrolyte. The converse of the above is also true; that is, if gas is bubbled through water, the gas takes a negative charge, while if the same gas is bubbled through a solution containing electrolytes, it takes a positive charge and the water becomes negative. Thus, it is a question of adsorption of ions at the gas-liquid interface. The same effects are produced when water is atomized or sprayed into air. In this case, if the water is of a high degree of purity, free from electrolytes, the small particles of vapor will become positively charged, while the charge in the case of electrolytes depends upon the concentration of the solution.

IONIC ADSORPTION

It is generally conceded that in the colloidal state particles carry an electrical charge, or in other words, there is a potential difference between the liquid and the micelles dispersed therein. Most evidence tends to show that it is the adsorption of ions upon the dispersed particles which gives them the charge. Very fine particles suspended in liquids adsorb free ions and the particles thereby become charged. They, therefore, behave somewhat like the ion itself. They will move under electrical stress towards the cathode, or negative pole, if the ion adsorbed is of a positive nature, and towards the anode, or positive pole, if the ion adsorbed is negative. Particles of silver bromide move to the cathode when peptized by silver ions, and to the anode when peptized by bromine ions. By following the migration of these particles with the ultramicroscope, the rate of movement of the suspended particle for a given difference in electrical potential may be determined. The rate of migration of colloidal particles under such electrical stress is of an order similar to that of the ions [12] Ellis and Powis [13] have studied the transfer of drops of oil under electrical stress and find that the migration velocity is usually from 3 to 4 μ per second

[11] Lenard, *Ann Phys* (3), 46, 584 (1892).
[12] Zsigmondy, "The Chemistry of Colloids," Wiley & Co., New York, 1917, p 46
[13] Ellis and Powis, *Z. Phys. Chem.*, 89, 91, 186 (1915).

It is largely through the electrical forces that the particles of suspension colloids are kept in a state of dispersion. The particles carrying like electrical charges all mutually repel each other, which, of course, is a factor in promoting stability While the exact reason for these electrical charges is not fully understood, it is more or less considered, however, that it is the adsorption of the ions upon the surfaces of the particles or micelle The adsorption of the ions is thought to be concentrated near the surface of the globules in a layer of the liquid immediately bathing the globules, and it is thought that there is a layer of oppositely charged ions on the outer film, that is, in the nearest vicinity to the outer phase or medium in which the particles are dispersed, which determines the character of the charge similar to the principle of a condenser. This is known as the Helmholtz double layer.[14]

As an illustration, in an emulsion the oil globule and its double layer may be considered as a small condenser. A definite potential difference exists between the oil and the nearer ionic layer, and in the oil-in-water type of emulsions, the ionic layer nearer to the water-phase is always negative. This can
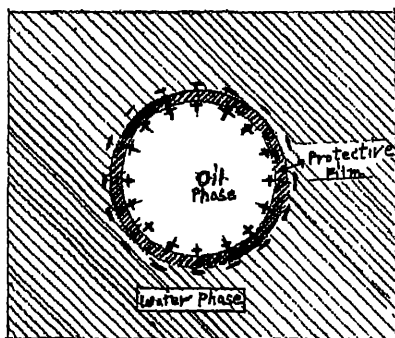
FIG. 3—Oil-in-Water Emulsion Showing Helmholtz Double Layer Effect.

be proven by the fact that all oil-in-water type emulsions migrate to the positive pole or anode when an electric current is passed through the dispersion The ionic micelle, which is believed to exist in the condition, as above described, with the Helmholtz double layer, of course migrates in the electrical field and is similar to the migration of an ion, but being of larger size, of course, its speed of travel is somewhat different, there being greater resistance.

CONDENSER EFFECT (HELMHOLTZ DOUBLE LAYER)

Assuming that a charged particle may be considered as a spherical condenser with the electrical double layer, it is possible to determine the rate of migration or velocity of the suspended article, and from this to calculate the potential of a charge on the particle, if the thickness of the double electric layer is known. Von Hevesy [15] has calculated that the thickness of this double layer is about 5 $\mu\mu$, and from this has calculated that the mean potential difference between an ion or a suspended

[14] Helmholtz, *Ann. Phys*, 7, 337 (1879).
[15] Von Hevesy, *Kolloid-Z.*, 21, 129 (1917).

liquid particle and the surrounding liquid is about 70 millivolts; also, that this potential difference will decrease when electrolytes are added, making the sol less stable, until the potential difference becomes zero at what is known as the isoelectric point However, experiments of Ellis and Powis [16] indicate that the coagulation tends to take place as soon as the calculated potential difference between oil drops and the liquid in which they are dispersed becomes less than 30 millivolts. In the case of oil-in-water type emulsions, this would be a negative difference of 30 millivolts, while with some solids dispersed in water, the charge is positive, so the potential difference would be plus 30 millivolts.

Helmholtz considered that under usual circumstances liquids and solids become charged electrically when brought into contact, the surface of the particle having the opposite charge from that of the liquid in which it is in contact, thus giving rise to this so-called double layer. He concluded that the charge of the double layer when in the liquid is about 0 1 $m\mu$ from the solid. He deduced this value from experiments with platinum wires in sulfuric acid.[17] McBain [18] contends, however, that since platinum is oxidized superficially by nascent oxygen, Helmholtz's conclusions must be wrong and the double layer must be thicker than that assumed by Helmholtz Helmholtz' conclusions of the double layer and the conditions similar to those existing on a condenser are in perfect accord with more recent discoveries and work along this line The fact that the ions are adsorbed upon the surface goes to support this theory. In order for them to set up a definite potential on the outer layer of the film, there must be an equal opposite charge on the other side of the film. Thus, the substance dispersed is really neutral, or the electrical charges are equalized by the double layer, but there would be a decided difference in potential between the outer film surrounding the particle and the liquid in which it is dispersed, hence the migration to the electrode when a current is passed through the dispersion In other words, regardless of what one may assume as to the double layer, the charge on a porous diaphragm depends upon the nature of the ion ad-sorbed. It therefore follows that an aqueous solution will flow one way or the other through a diaphragm depending upon the nature of the dissolved substance. This has been brought out clearly by Perrin,[19] who found reversal in cases where the solutions were alkaline

EFFECT OF DIELECTRIC CONSTANT

Every diaphragm tends to become charged positively in an acid solution and negatively in an alkaline solution, and every ion of unlike sign

[16] Ellis and Powis, *loc. cit*, p. 186.
[17] Helmholtz, *loc. cit*
[18] McBain, *J. Phys. Chem*, **28**, 706 (1924).
[19] Perrin, *J. Chim Phys*, **2**, 601 (1904).

tends to neutralize the charge of the diaphragm. Perrin is of the belief that the effect of other ions is more marked the greater the valency. By keeping the colloidal particles stationary in a porous diaphragm so that they cannot move in any definite direction, the water will move to the cathode when the diaphragm is made of glass, shellac, earthenware, asbestos, wool, cotton, etc. When turpentine is substituted for water it moves to the anode. Coehn has accounted for this by the fact that two non-miscible substances are in contact, one being a pure liquid, and the substance with the higher dielectric constant is charged positively with reference to the one with the lower dielectric constant. From this, however, one can readily appreciate that the dielectric constant is an important factor in determining direction of migration This seems to be borne out when one considers that in all oil-in-water type emulsions, the dispersed oil globules migrate to the positive pole, that is, carry a negative charge Lewis made quite a series of these emulsions by various means and obtained them in diameters of about 0 4 microns, and found that they invariably were negatively charged, that the potential difference of the double layer (Helmholtz effect) was 0 05 volts, and that the measurement of the size of the charge on the droplets by the electrophoresis method indicated $4 4 \times 10^{-7}$ electrostatic units

On the addition of an electrolyte the charges on the dispersed globules or particles are neutralized, and being electrically neutral, they coalesce or are precipitated. The active agent in the precipitation is, of course, the ion with the opposite charge to that of the suspended particles, being so either in the case of emulsions or suspension of solids

Oppositely Charged Suspensions, or Neutralizing Effect

Neisser and Friedmann,[20] also Baltz,[21] have found that suspensoids with like electrical charges do not have any appreciable effect on each other when brought in contact, but that suspensoids with opposite electrical charges precipitate each other. Thus, if negative sols are added to negative, or positive to positive, there is no precipitation, but when a negative sol is added to a positive, it always results in precipitation. For instance, gelatin in an acid solution, and therefore bearing a positive charge, is precipitated by tannin, which has a negative charge This principle is used in the tanning of hides, the collagen of the hide absorbing tannin and becoming leather.

The suspension colloids, or suspensoids, are easily precipitated by small quantities of electrolytes, while the so-called emulsion colloids, or emulsoids, are not easily precipitated except with higher concentrations of salts or electrolytes when the colloid is partly dehydrated or salted out

[20] Neisser and Friedemann, *Munch. Med. Wochenschrift*, No. 11 (1903).
[21] Baltz Ber 37 1095 (1904)

Some reagents such as alum, ferric chloride, basic lead acetate, etc , readily precipitate colloids, and for this reason are spoken of as clarifying agents. The active precipitating agent is the ion with the opposite electrical charge to that of the colloids, and its precipitating action varies greatly with its valency. The precipitation of colloids by electrolytes is the opposite action to that of peptization. The colloids do not precipitate in a compact form, such as crystalloids do, but in more or less of a swollen or hydrated condition.

The sign of the charge on the dispersed particle depends upon the medium in which it is dispersed. Most particles when dispersed in turpentine take on a positive charge, while in water a greater number take on a negative charge. The dielectric constant, of course, is a factor in this case.

What is known as irregular series have been observed,[22] when suspensions of a positively charged colloid are added to suspensions of those negatively charged, and cases of reversal in charges have occurred, which are probably due to the adsorption of ions carrying the opposite charge to a point where they predominate. We know, however, that cases of adsorption are not limited to colloids having opposite signs, for instance, charcoal adsorbs both bases and acids.

Schultze[23] pointed out years ago that small amounts of gelatin solutions were as effective as lime or alum in causing rapid sedimentation of clay, and that small additions of gelatin to barium sulfate simplified the filtration and washing very much   Billitzer[24] found that gelatin precipitates such negative colloids as antimony sulfide and arsenious sulfide in acid or neutral solutions. Gelatin in ammoniacal solutions will precipitate hydrous ferric oxide, but a precipitation does not occur when ammonia is added to a mixture of gelatin and ferric oxide.

Coagulation of Colloids

The general principles governing the coagulation of a colloidal solution by mixture of electrolytes are theoretically very simple[25]   The applications in an individual case are not necessarily easy, because we have to contend with the precipitating action of mixtures of electrolytes the effect of the presence of each precipitating ion on the adsorption of the other, and the stabilizing action of ions which have a charge similar to that of the colloid   The amount of a sol necessary to precipitate another sol of opposite charge will vary with the degree of adsorption, and the coagulating material will adsorb more or less of the coagulating

[22] Freundlich, "Kapillarchemie," Akademische Verlagsgesellschaft, Leipzig, 1909, p 409
[23] Schultze, *Pogg Ann*, 129, 369 (1866)
[24] Billitzer, *Z phys. Chem*, 51, 145 (1905)
[25] Weiser, *J Phys Chem*, 25, 665 (1921); also *J. Phys Chem*, 28, 232 (1924)

salt, which, of course, will mask the theoretical results.[26] The degree of instability varies greatly from one colloid to another and with the method of preparation. So long as the particles all carry a similar charge, they will tend to repel each other and will not coalesce unless the concentration of the electrolyte is too high. If this is neutralized, however, the particles will agglomerate unless some other factor comes into play For instance, if the solution contains peptizing ions, these will offset, to a great extent, the action of the ions with opposite charge which tends toward precipitation.

Take an aqueous suspension in which the particles are charged positively. The water would, of course, have a negative charge. The positively charged colloidal particles attract the negatively charged electrolytes and the charges on the particles are thus neutralized. This gives surface tension a chance to draw these particles together and form a precipitate. Some of the electrolyte present is usually carried down with this precipitate and is not easily removed by washing. We have, then, two forces acting counter to one another, and it is easy to understand the action of electrolytes in causing precipitation. When these colloidal solutions are exposed to the air, for instance, which contains a large number of electrolytes, these are adsorbed on the surface of the solution. An example of this is the action of carbon dioxide upon emulsions. It is found that if exposed to fairly stable emulsions, air which has present considerable quantities of carbon dioxide will affect these emulsions considerably. This is especially noticeable at higher temperatures and is not such a factor below 15° C.

When two oppositely charged sols are dispersed in pure water, there is an amount of one which is equivalent to that of the other and which will just precipitate it. When these two sols are put together in electrolytically equivalent quantities, or when an electrolyte is added to a sol in just a sufficient quantity to neutralize the charges, we arrive at what is known as the isoelectric point; in other words, the point at which we have neutralized the charges on the sol. This is the condition of most unstable equilibrium and is the point we usually try to avoid in the production of colloidal dispersions. To promote stability in dispersions, it is necessary to determine which type of charge the dispersion has, then add a substance which will increase the type of charge desired for stability. In other words, it is advisable to have oil-in-water types of emulsion, which carry negative charges, slightly on the alkaline side, so that the hydroxyl ion will be adsorbed on the surfaces of the micelles and assist in promoting stability

This principle plays an important part in dyeing, due to the fact that mordants are frequently added to render the color more permanent For instance, aluminum chloride, acetate, etc , hydrolyze in the presence

[26] Bancroft, *op cit.*, p. 292.

of the water and form colloids. These colloids react with the dyes, and if they have a charge opposite to that of the dye, the mordant and the colloidal dye are precipitated in the fibers of the fabric.

ELECTRICAL ENDOSMOSIS

If semi-porous membranes are inserted in a colloidal solution, and an electrical current is set up through the membrane, a flow of liquid will pass from one side of the membrane to the other, the direction of flow depending on the charge on the diaphragm. This is known as electrical endosmosis.[27]   Girard [28] has confirmed the results as to reversal of flow when changing from an acid to an alkaline solution. Very dilute acids flow to the anode; alkalies to the cathode. The colloids are precipitated on the anode or cathode according to the charge on the particles and the liquid can be made to flow in the opposite direction through the membrane, while the colloids, of course, will not pass through. This principle has been applied in industrial operations for the rapid removal of water, and a great number of patents have been taken out for the removal of water from clay, etc , and for the separation of colloids from closely associated crystalloids which may pass through the membrane when in solution.

The amount of liquid transferred by electrical endosmosis increases with rising temperature, the increase being nearly proportional to the change in fluidity. In electrical endosmosis the diaphragm probably becomes charged, due to an adsorption of ions on the membrane; the flow of liquid is usually from the anode to the cathode, but may be in the reverse direction, depending to a great extent upon the charge on the diaphragm. The phenomenon must not be confused with ordinary electrolysis when a current is passed through a crystalloid solution. In using this method for the removal of liquids from colloidal dispersions, it is necessary to consider the charge on the colloidal particles in order to determine on which side of the membrane the dispersoid should be placed. The electrical phenomena in non-aqueous solvents are in many cases more complex than in water   For instance, Perrin [29] found that electrical endosmosis did not occur in solvents such as carbon disulfide, chloroform, ether, benzene, etc., but he observed pronounced endosmosis in solvents such as water, methanol, acetone, nitrobenzene, etc. This latter class of solvents, however, has high dielectric constants, and therefore, great dissociating power, so that this relation is of interest. The solvents with high dielectric constants show very pronounced electrical properties.

[27] Reuss first discovered endosmosis in Moscow in 1809
[28] Girard, *J. Chim Phys.*, 17, 383 (1919).
[29] Perrin, *Compt. rend*, 136, 1388 (1903)

Boudouin [30] has shown that when substances in water are positively charged, they also have a similar charge in methanol, a liquid of high dielectric constant. He has also shown the reverse to be true. For instance, substances which have a positive charge in water will usually have the reverse charge when dispersed in turpentine. This directly leads back to the question of dielectric constant.

CATAPHORESIS

The movement of liquids through diaphragms and capillary tubes under an impressed electromotive force has been discussed under electrical endosmosis. The movement of solid suspended particles through the liquid in which they are suspended, under the action of an external electromotive force, is known as cataphoresis. This migration of suspended particles to the electrode in a sense is analogous to the migration of ions in a true solution when an electrical current is passed through such solution. While the conductivity of the colloidal particles is small, it is much greater than that of the water in which they are suspended. This raises the question whether this conductivity is not due to electrolytes adsorbed on the colloidal particles. This question is not yet settled. However, these electrolytes are held so firmly to the colloidal particle that they cannot be separated by dialysis. In moving to the electrodes they, of course, must carry electrical charges and take part in the conduction of the current through the liquid

The determination of the velocity with which the particles move in cataphoresis is not a very difficult matter, as the method is similar to that employed in determining the absolute velocities with which the ions move in true solutions. Electrodes are inserted into two ends of a vertical tube containing the sol, and the current is passed in the direction so that the colloids will move to the electrodes in the lower end of the tube. In settling, they possess a sharp upper surface which can readily be seen, with sufficient accuracy so that the distance through which it settles in a given time, with a given fall in potential, is easily measured.

Cataphoresis is made use of in electrolytic refining, also in plating generally with the use of additional agents It seems to be useful in the purification of clay There is also an interesting commercial application in connection with emulsions, due to the fact that all oil-in-water types of emulsion carry a negative charge. When such an emulsion is made of blown oils of asphaltic origin, these will migrate to the anode or positive pole Hence, if one wishes to plate out these products on the anode, it is readily accomplished by passing a current through the emulsion, the oil globules will migrate to the anode and deposit thereon. The anode is then removed and baked This is a new process of japanning

[30] Boudouin, *Compt rend,* 138, 898 (1904)

and it seems to work very satisfactorily,[31] giving an even plating The thickness of the layer can be quite readily controlled, and one of the decided advantages is that the current density, which is so important in all electroplating of metals, does not make a great deal of difference here. Any current from 10 volts to 110 volts seems to plate out satisfactory.

Another application which has a promising future in industry is the cataphoresis of rubber latex for the making of what is known as anode rubber. This rubber, plated out on the anode, due to cataphoresis, has many times the tensile strength of rubber obtained by the usual flocculating or coagulating methods, and apparently has quite a promising future.

Cataphoresis removes all doubt that particles in a so-called colloidal state of dispersion carry electrical charges, but as stated many times, the origin of this charge is still open to question. The electric charge is believed to be due to the adsorption of ions, and in emulsions which carry a negative charge, the adsorption of hydroxyl ions at the surface of oil globules is postulated. Hydroxyl ions are always present, due to the ionization of the water.

ELECTRICAL CONDITIONS AFFECTING THE STABILITY OF COLLOIDS

The electrical charge of agar, starch, gelatin, or other emulsoids may be fully taken away without causing coagulation. If electrolytes are added in sufficient amount to flocculate a suspensoid sol no flocculation occurs, although the particles have lost their charge, which can be observed by cataphoretic measurements. The electrical charge, however gives an increase in the viscosity of the sol and is frequently spoken of as the electroviscous effect.[32] The reason this discharged emulsoid sol does not coagulate cannot be sought in the probability of collision, which cannot be greatly different from that of a suspensoid sol. Therefore, there must be some factor maintaining the stability of the sol by lowering the possibility of adhesion when no electrical charge is left This is obviously the hydration of the particle, for when the sol is discharged or electrically neutral, it flocculates as soon as dehydrating substances such as alcohol, sulfuric acid, acetone, etc., are added Therefore, such salts as magnesium sulfate can cause flocculation or salting out by first discharging and then dehydrating the particles. When alcohol is added to cause complete dehydration, and the particle is allowed to remain charged, no flocculation occurs, the sol merely changing its character from lyophilic to lyophobic.

These results lead to the conclusion that the probability of adhesion

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[31] Davey, "Making and Breaking of Emulsions," Colloid Symposium Monograph, Vol 4, Chemical Catalog Co , New York, 1926.
[32] Kruyt and Eggink, *Proc Roy. Acad (Amsterdam)*, 26, 43 (1922)

in a lyophilic sol (water sol) is not only dependent upon its electrical charge but also on its hydration, both of which assist in counteracting adhesion, hence we can speak of critical potential for a sol.[33] Stability depends upon its electrical charge and critical hydration. A sol depending only on its hydration is not very stable. Hence, to get permanent stability in a sol it is advisable to have both conditions correct In such case, the degree of discharge necessary to cause flocculation will be dependent also upon the hydration present; on the other hand, the degree of hydration will be dependent upon the charge present.

In order that a cation or anion may neutralize the charge on the colloidal particle it must be adsorbed, for we know that when colloidal particles are precipitated, some of the electrolyte is carried down with the precipitate and cannot be removed by any amount of washing. The idea that hydrogen and hydroxyl ions confer their electrical charge to colloidal particles on account of their great velocity and thereby are readily adsorbed by the colloidal particles is popular.[34] The hypothesis of a preferential adsorption of hydrogen and hydroxyl ions by colloidal particles has played an important rôle in colloidal chemistry.

Hardy[35] gives an interpretation of the influence of hydrogen and hydroxyl ions on the direction of migration of protèin particles in an electrical field. This has played an important rôle in colloidal chemistry, and has suggested to later workers that the hydrogen and hydroxyl ions produce their influence on an electrical charge of the protein particles through preferential adsorption.

THE ISOELECTRIC POINT

The isoelectric point[36] is found to be of great importance, for when this point is approached, the stability of the hydrosol diminishes and when reached, coagulation by precipitation readily occurs, according to whether the isoelectric point is reached slowly or quickly, with or without mechanical agitation.

It is possible to determine the charge on particles by observing their behavior in an electrical field. When a current is passed through the liquid between two electrodes, the positively charged particles will, of course, migrate to the cathode or negative pole, while the negatively charged particles will migrate to the anode, as described under cataphoresis Take the case of albumin dispersed in water When a trace of alkali is added, the albumin becomes negatively charged and will migrate to the anode; while in a slightly acid solution, the particle

[33] Kruyt, in Alexander's "Colloid Chemistry," Vol. 1, Chemical Catalog Co, New York, 1926, p. 321.
[34] Perrin, *J. Chim Phys.*, 2, 601 (1904), 3, 50 (1905).
[35] Hardy, *J. Physiol.*, 29, 203 (1903)
[36] Hardy, *Z phys. Chem.*, 33, 285 (1900)

becomes positively charged, and will migrate to the cathode. There is a neutral point at which the albumin will not migrate to either pole; this was termed the isoelectric point by Hardy. Other substances, of course, behave similarly. This demonstration is usually made with one of the emulsoid group, such as gelatin, albumin, and other protein substances.

The isoelectric point is a definite constant which can be measured with great accuracy in terms of hydrogen-ion concentration. The method of making hydrogen-ion determinations is fully discussed elsewhere (p. 80).

The nature of the charge on a colloid may be determined by comparing the various concentrations of electrolytes required to produce turbidity or approach the isoelectric point. For instance, factory wastes in streams are frequently precipitated by the use of alum. This can be effected because a large number of suspensions of solids in water carry a negative charge The Al^{+++} in alum, with its positive charge of 3, neutralizes the negative charge, thus causing the precipitation. On the other hand, the sulfate ions in alum are adsorbed by most colloids, which, of course, tends to peptize or help dissociate negatively charged aggregates. This peptizing action is partly chemical and partly electrical, one ion of the electrolyte being adsorbed by the colloid. The influences of the hydrogen ions and hydroxyl ions, however, are the most marked; that is, acids and alkalis are more active. With salts, the most active ion is that having the opposite sign to the colloid, and its effect is governed by the valency of the ion, as pointed out above in the case of aluminum in alum In peptizing actions, monovalent ions are more active than divalent or polyvalent; for instance, sodium is more active than barium, and barium is more active than aluminum. The same relations manifest themselves again with regard to precipitation Essentially the same amounts are required for cations of the same valence. The amount of any cation necessary to effect precipitation is primarily a function of its valence. Furthermore, the experiments show that all the salts with anions of the same valency act alike quantitatively and that all salts with cations of the same valency act alike on the alkaline side of the isoelectric point

PRECIPITATING EFFECT ON THE MICELLE

A transference of electrolytes can take place when colloids in dispersion containing adsorbed electrolytes are treated with another solution also containing electrolytes This means that the original cations adsorbed by the micelle can be replaced by a second electrolyte, which are similarly adsorbed by the colloid, the different ions from those combined with the colloid being adsorbed in replacing the former ones. That is' why the precipitating quantities of ions with different valence

are not proportional to their valency. As an illustration of this transference of electrolytes, Svedberg [37] states that the concentrations of K^+, Ba^{++} and Al^{+++} required to agglomerate particles of arsenic trisulfide to the same degree stand in ratios of $1.20:1000$. It is observed therefore that the precipitating values do not increase in direct proportion as the valency increases, but in far greater proportion.

To put the matter more generally, the amount of electrolyte required to precipitate a colloidal solution varies with the nature of the cation, the anion and the dispersed phase. Thus, it is generally true that ions of higher valency will be more strongly adsorbed than those of lower va'ency, as illustrated in the example given above. This is known as Schulze's law.[38] Kruyt and van der Speck [39] found that the precipitation value of potassium chloride decreases when we decrease the concentration of the colloid, while the precipitating value of barium chloride does not change appreciably with the dilution

From the study of influence of hydrogen-ion concentration on the stability of sols toward electrolytes Tartar [40] concludes "that the precipitating value of all electrolytes for a given colloid is approximately the same when they are all treated under the same hydrogen-ion concentration," in other words, when they are all treated under the same conditions. The hydrogen-ion concentration factor, of course, must not be overlooked, otherwise the conditions are radically different.

At the isoelectric point the various proteins which are used as emulsifying agents or protective colloids behave in a peculiar manner. When they pass into so-called solution, it is usually turbid and always unstable. A precipitate forms in time, or immediately on addition of certain reagents which dehydrate them, such as salts, alcohol, etc. The addition of a small quantity of acid may cause the liquid to clear, while a larger amount may cause precipitation, or a small quantity may cause precipitation and a larger quantity peptization. Similar effects are produced by alkali, depending upon the particular colloid dispersed. The mineral matter associated with the colloids is retained by them, and after treatment with water and long continued dialysis a portion may be removed, but the greater part still remains unaffected The greater part of the mineral matter may be extracted by treatment with weak acids to remove the bases, followed with weak alkalies to remove the acids and washing with many changes of water These are sometimes spoken of as colloidal electrolytes and are salts in which one of the ions is replaced by the ionic micelles. They are highly charged and solvated colloidal particles.

[37] Holmes, "Laboratory Manual of Colloid Chemistry," Wiley & Co , New York, 1922, p 22
[38] Schulze, *J Prakt Chem.* (2), **25**, 431 (1884)
[39] Kruyt and van der Speck, *Koloid-Z*, **25**, 3 (1919).
[40] Tartar and Gailey, *J Am Chem. Soc*, **44**, 2212 (1922).

A typical example of this is soap when in so-called solution in water. Under such condition colloidal particles may conduct much better than true ions. Bancroft [41] states that the actual conductivity of an ionic micelle containing, for instance, ten palmitate ions, is perhaps twenty or thirty times that of a single palmitate ion. Thus, the equivalent conductivity 'of the ionic micelle is several times greater than that of the simple fatty ion.

REMOVAL OF MINERAL MATTER

Mineral matter can be removed at the isoelectric point because neither acids nor bases combine with the micelle An example of this is the preparation of isoelectric gelatin as worked out by Loeb [42] This consists in steeping the gelatin in dilute acetic acid of $N/40$ strength and washing numerous times with ice-cold water. After the mineral matter has been removed, the colloids behave quite differently. Therefore, the mineral matter cannot be regarded as an impurity in natural colloids but is combined with them and largely constitutional, the properties of the colloids being greatly dependent upon its presence.

The first to consider the phenomena of coagulation, especially the silica phenomena studied by Graham, observed that these fixed impurities were eliminated by dialyzing the colloids. The micelle greatly increases in size, however, and the colloid is far more susceptible to coagulation by electrolytes, changes of temperature, etc, and when coagulated, become irreversible.

The statements above are not always true, for dialysis does not always make colloids unstable For instance, those made electrically are quite resistant to dialysis, and in some instances the electrolytes are necessary for even the existence of the colloid. However, it is not necessary to have one certain electrolyte, as the important point is the electric sign of the stabilizing electrolyte. At the isoelectric point certain colloids have their physical properties greatly suppressed and their stability is very slight The above indicates that these colloids cannot be dealt with on a purely chemical basis. Even some of the laws of pure chemistry and also chemical forces themselves are now being explained on a different basis, due to recent work of physicists on atomic structure.

STABILIZATION AND PRECIPITATION

We have thus far devoted most of our attention to the ion of the precipitating electrolyte, which has the charge opposite to that of the

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[41] Bancroft, *op cit.*, p 305
[42] Loeb, "Proteins and Theory of Colloidal Behavior," 2nd ed., McGraw-Hill Book Co., New York, 1924, p 33, 40, 42

colloidal particle. We must not, however, ignore the electrolyte having a charge the same as the colloid, for this has the property of rendering the colloid more stable Thus the hydroxyl ion increases the stability of negative sols and the hydrogen ion increases the stability of the positive sols. However, in salts this effect is so small in comparison with the precipitating action of the oppositely charged ions, that the latter is always more strongly dealt with

Taking all these factors into account, that is, adsorption, protecting effect of ions of the same sign, etc, it can readily be appreciated why the quantities of ions of different valence are not proportional to their valencies, as previously pointed out There is a great amount of research still to be done in this direction.

The principle of stabilization and precipitation of colloids is not confined to dispersions in liquids, but is of equal importance in the case of dispersion in gases or what are known as aerosols, for these particles are in a charged condition also A recent application of this principle was the attempt to disperse fog or clouds. Sand containing opposite charges was sprayed on the clouds to those on the particles, thus releasing the charge and as a result the small droplets in the fog or cloud coalesced, which, of course, was followed by precipitation. This operation was briefly described in the *Scientific American* for January, 1925, under "Methods of Dispelling Fog" The work was based on the assumption that visible forms of moisture in the air, like mist, fog or clouds, are a form of colloidal suspension in gases and that they should be governed by the same general laws that prevail in colloidal dispersion in liquids. In other words, the droplets of fog or clouds are so small that gravity does not act upon them, due to the friction of the surrounding air, which is in agreement with Stokes' law. This demonstration is merely pointed out to show some of the popular applications of these principles.

For sols of constant composition, the precipitating value is greater when the electrolyte is added slowly over a long interval of time than when added all at once [48] and this effect is more pronounced with univalent precipitating ions. This is an important point and must be considered in problems involving precipitation.

The addition of electrolytes to some sols results in appreciable sensitization Billitzer [44] found that negatively charged platinum sol could be discharged and even charged in a positive direction by the suitable addition of alcohol In such a case, of course, it must be recalled that with a metallic sol the question of hydrolysis does not enter in so much. For instance, Klein showed that negatively charged sols of arsenious sulfide, silica, and ferric oxide were agglomerated in part by

[43] Freundlich, *Z. phys. Chem*, **44**, 143 (1903)
[44] Billitzer, *Z. phys Chem.*, **45**, 312 (1903).

alcohols, whereas positively charged ferric oxide and silica were not. On the other hand, Freundlich and Rona [45] observed that the addition of camphor, thymol and urethanes to ferric oxide sol reduced the precipitating concentration of electrolytes required. This sensitization of sols by non-electrolytes was attributed by Cassuto [46] to a change in the dielectric constant of the medium in which the sol was dispersed. It would seem that the addition of colloids or non-electrolytes having lower dielectric constant than water will always decrease the precipitating value of the electrolytes and that this effect is greater the lower the dielectric constant of the non-conductor added

IONIC ADSORPTION ON THE MICELLE

The point of view taken by some writers is that a colloidal micelle is similar to a large molecule.[47] They even go so far as to state that its properties are similar to a salt molecule That is, if the dispersion medium is an ionizing one, this micelle is ionized as the result of the hydrosol, hence is a conductor of electricity. In other words, the ionization of the micelle is similar to that of a molecule and depends upon the degree of ionization. This view is not held by a great number.

There are a great number of amorphous substances which form negative colloids under practically all conditions. These include the silicates, the resins, the higher fatty acids, etc. There are also a great number of colloidal ions such as albuminous substances, taking in albumin, glue, silk, wool, and metallic hydroxides, in which the charge depends to a large extent on the hydrogen-ion concentration The isoelectric point of these substances occurs either on the acid or alkaline side. With a large number of the albuminous substances it is on the acid side, while with the hydroxides it is on the alkaline side. On the other hand, no amorphous substances have been discovered up to this time which form positive colloidal ions under all conditions. Some of the metal oxides, such as AgO and Na_2O, dissolve in the ionized form; in these cases colloidal ions do not have a chance to form It is believed by a great number that there are no independent ions of colloidal substances, that is, that the silicates or silicic acids in general are only peptized and that it is largely a question of adsorption of other ions which regulates the charge on the particles It is also believed that there are free valence bonds existing at the surface layer of atoms of the crystals and that ions are adsorbed by these bonds and tie together oppo-

[45] Freundlich and Rona, *Biochem Z.,* **32,** 81, 87 (1917).
[46] Cassuto, "Der kolloide Zustand der Materie," Verlag von Th Steinhopf, Dresden, **1923,** p. 152.
[47] Duclaux, *Compt. rend.,* **140,** 1458 (1905).

sitely charged ions.[48] In other words, each surface of a crystal, or in fact, a surface of any sort, possesses adsorptive power for ions.

It is true that an individual micelle behaves under the influence of an electric current in many respects similar to the individual molecule of a dissolved electrolyte, but there is the electrical double layer to consider and there is a space in this double layer between the moving positive and negative particles When an electrolyte goes into true solution, the molecule is split into individual ions, while in the case of a colloidal micelle the double layer is split into two sections.[49] Of course, in both cases the carriers of opposite charges move in different directions when an electric current is passed through the liquid, and they move under the influence of the external electric force. This movement in true electrolytes is spoken of as conduction, and in colloidal dispersions is called cataphoresis The colloidal micelle might be looked upon as a gigantic molecule having attached to it equivalent quantities of the ordinary ions of opposite charge. McBain[50] has demonstrated this mechanism on soap solutions in a very clear manner: here the monovalent metals, such as sodium, combine with the lower fatty acids to form the salts, and as the carbons in the fatty acid series are increased the soap assumes more and more colloidal properties when dissolved in water

DIFFERENCE BETWEEN AN ELECTROLYTE AND A MICELLE

True electrolytes such as common salt break up into independent ions with simple elementary charges, according to definitely established laws with a definite number of electrical charges conducted to the electrodes. This is so exact that we can calculate accurately just how much electricity is conducted[51] under standardized conditions. This is not the case with colloidal particles when cataphoresis is performed. The electric charge on colloidal particles is generally traced to the electrical double layer, and involves the question of what is the inner mechanism, or chemistry, by which this arrangement of electrical charges is brought about. This probably takes us to the study of the electron, which is discussed more fully in another chapter (Chapter III).

It is well to bear in mind that a great number of colloids can be discharged by the addition of electrolytes, and when the concentration of the electrolytes is increased, a point is finally reached at which the charge on the colloidal particles is zero under a definite hydrogen-ion concentration. The particle is then at what we speak of as the isoelectric

[48] Freundlich, *op. cit.*
[49] Michaelis, in Alexander's "Colloid Chemistry," Vol 1, Chemical Catalog Co., New York, 1926, p 492
[50] McBain, *J. Am Chem Soc.*, 42, 426-60 (1920).
[51] Faraday's Law, *Exper Researches*, III, Ser. No 373 (1832)

point for the given colloid. This seems to point quite strongly to the electrical double layer theory.

We also know that the so-called solubility of the colloid, which is really peptization, is largely a matter of the adsorption of ions on the surface. Hence, it does not seem as though we get the true viewpoint when we look upon colloids as similar to electrolytes. While they both migrate to one pole or the other when an electric current is passed through the liquid, nevertheless, there are decided differences in their properties and their characteristics, as pointed out above, and the evidence goes to indicate that adsorption plays a prominent rôle in colloidal substances. Furthermore, from evidence disclosed in Chapter III, it looks as though it is necessary to go back to the electron to get a clearer conception of why these electrical charges on the micelles play such an important part in all cases of mechanical dispersion, deflocculation, emulsification, etc.

Not only do these questions enter into deflocculation, but also into a great amount of the work on filtration, and they are certainly going to play a prominent part in the preparation of various colloidal materials. —more so in the future than in the past. It is these factors which make one realize the importance of the theoretical end of the work, its importance being far greater than the machine or equipment end, for without the proper conditions in the process, the machine or other equipment will be of very little aid.

Chapter VII.

The Meaning of Hydrogen-Ion Concentration and Its Importance in Colloidal Dispersion.

The older methods of detection of acidity and alkalinity by means of such indicators as litmus, phenolphthalein, and the like, are, of course, well known. By these means, however, a measure of the active acidity or alkalinity of the solution is not obtained, for the degree of acidity or alkalinity is governed by the hydrogen or hydroxyl ions present in a solution. This is the true method of registering chemical activity and eliminates the old idea of strong and weak acids, which is very indefinite and is a matter of personal opinion By strong acids, what is really meant is a highly dissociated solution It is the hydrogen ions in solution which determine the acidity, while it is the hydroxyl ions in solution which determine the alkalinity. To illustrate this point in a better manner, hydrochloric acid is usually classified as a strong acid, while acetic acid is classed as a weak acid. Yet these two acids, when made up to the same normality or chemical equivalent strength, would in each case neutralize the same amount of alkali of the same normality, for this is the basis of making up the normal solutions. By hydrogen-ion determinations it is easy to demonstrate that the hydrochloric acid of the same *normality* is over sixty times as strong as the acetic acid *in relation to its hydrogen ions,* and that is what determines the chemical activity, as explained under electrolytic dissociation.

In order to explain more what is meant by hydrogen-ion dissociation for those who have not heretofore used this method of control, it is, perhaps, advisable to explain the theory and practice more in detail A clearer conception of just what is meant may, perhaps, be brought about in the following way· Pure water is formed theoretically by the combination of equal numbers of hydrogen and hydroxyl ions. It is easily determined that pure water is only slightly dissociated, so slightly, in fact, that under ordinary conditions it is practically negligible Hence, hydrogen and hydroxyl ions cannot remain in the presence of each other, to any extent, uncombined. It is not too much to state that a great percentage of chemical reactions owe their existence to this fact

MASS ACTION

According to the theory of electrolytic dissociation, when the hydrogen and hydroxyl ions are exactly equal in number, the solution is neutral. If the number of hydrogen ions is in excess of the hydroxyl ions, the solution is acid; on the other hand, if the solution contains an excess of hydroxyl ions, it is alkaline.

According to the law of mass action, for any solution, the product of the ion concentrations, divided by the undissociated parts, or those in the molecular state, will remain constant, provided the temperature is kept constant. In mathematical form, this is as follows, for water:

$$\frac{\text{Concentration of H ions} \times \text{concentration of OH ions}}{\text{Concentration of undissociated portion}} = a \text{ constant}$$

In brief form:

$$\frac{\text{Conc. } H^+ \times \text{conc } OH^-}{\text{Conc. } H_2O} = K$$

As previously stated, the proportion of the water undissociated being predominant, it may be considered as a constant with respect to the small product of the dissociated ions in the numerator, so that the equation can be brought to the following form:

$$\text{Conc. } H^+ \times \text{conc } OH^- = K.$$

From the above law, it is quite obvious that an increase in the hydrogen ions entails a decrease of the hydroxyl ions, and vice versa, in order for the product to remain constant. Now, by measuring the conducive power of water, the constant has been found to be $\frac{1}{100,000,000,000,000}$ or 10^{-14}. Since the number of hydrogen and hydroxyl ions in the case of pure water are equal, the single proportion of each must amount to $\frac{1}{10,000,000}$ or 10^{-7}.

SORENSEN'S pH SCALE

For practical use these figures are very cumbersome, and in order to avoid them a method has been devised of using powers of the numbers. By establishing the base as 10, the exponent or power of 10 becomes the logarithm. We do not reckon with the negative sign of the exponent, that is, with the negative logarithm of these powers, and as an indication in this abbreviated method, we use the expression pH. The pH value is the exponent of hydrogen-ion concentration, and instead of saying $H^+ = 10^{-1}$, we say $pH = 1$. This method was first suggested by

Sorensen, is usually spoken of as Sorensen's logarithmic scale, and has now been generally adopted.

In the case of pure distilled water, where the hydrogen-ion concentration is $N/10,000,000$ or $0.0000001N$, the pH value would be the logarithm of $1/0.0000001$, which is 7.0. The value of 7 is the neutral point of the pH scale. Values below 7 indicate acidity, the degree of this acidity increasing as the numbers decrease, for the mathematical reason given above. For instance, if a small amount of acid is added to distilled water, this acid will dissociate. For instance, if we added hydrochloric acid, we would have dissociation into the positive hydrogen ions and the negative chlorine ions. Hence, the total number of hydrogen ions in the solution would be in excess of the hydroxyl ions, due to the addition of the acid, and the solution would, of course, become acid. If the hydrogen-ion concentration were found to be $N/1,000,000$, the pH value would be the log of 1,000,000, which is 6. Similarly, if the hydrogen-ion concentration were $N/100,000$, the pH value would be 5. Since we are dealing with logarithmic values, a solution having a pH value of 5 is 10 times as acid as one with a pH value of 6, while with a pH value of 4 it is 10 times as acid as a pH value of 5, etc.

By the law of mass action it is apparent that when the hydrogen-ion concentration increases, the hydroxyl ion must decrease, in order to maintain the constant. Hence, even in a strongly alkaline solution hydrogen ions exist, even though they are neutralized, so for the sake of simplicity it is advisable to express both alkalinity and acidity in terms of pH value. From the fact that neutral water has a hydrogen-ion concentration of 7, it is apparent that alkaline solutions must contain a smaller number of hydrogen ions in order to maintain the constant. By adding small amounts of sodium hydroxide to water, we decrease the hydrogen-ion concentration, and if this were decreased to the point of $N/100,000,000$, the pH value of such a solution would be 8. If the hydrogen-ion concentration were reduced again by adding more alkali so that it had a value of $N/1,000,000,000$, the pH value would be 9. Hence, all values higher than 7 indicate alkalinity, and due to the fact that pH is based on logarithmic scale of reciprocal numbers, the degree of alkalinity increases as the pH value increases. Each time the pH value increases one unit, the solution increases ten times in alkalinity. When the method of measuring hydrogen-ion concentration was developed by Friedenthal and Sorensen,[1] it became possible to determine the isoelectric point of genuine proteins. This was first done by Michaelis[2] in 1910, and the method used was the migration of particles in an electrical field, the isoelectric point being the hydrogen-ion con-

[1] Loeb, "Proteins and the Theory of Colloidal Behavior," 2nd ed., McGraw-Hill Book Co., New York, 1924, p 9.
[2] Michaelis, "Die Wasserstoffionenkonzentration," Berlin, 1914, p. 54.

centration at which the particles will not migrate to the anode or cathode The hydrogen-ion concentrations of some of the typical proteins at the isoelectric point, as determined by Michaelis, are as follows ·

		Normality
Genuine serum albumin ...	... .	2×10^{-5}
Genuine serum globulin	4×10^{-4}
Oxyhemoglobulin	12×10^{-7}
Gelatin	2×10^{-5}
Casein	2×10^{-5}

IMPORTANCE OF HYDROGEN-ION CONTROL

Loeb [3] has performed a great number of experiments which bring out clearly the importance of considering hydrogen-ion concentration, especially with work on gelatin. The isoelectric point of gelatin has a hydrogen-ion · concentration of $2 \times 10^{-5} N$, or pH 4.7 according to Sörensen's logarithmic notations. According to Loeb, on the acid side of the isoelectric point only anions of neutral salts are taken up, while on the alkaline side only cations are taken up. After Loeb had performed a great number of experiments on hydrogen-ion concentration, he stated that, in his opinion, it was an unfortunate historical incident that work on colloidal dispersions had developed so far before considering hydrogen-ion control, otherwise the history of this new science would be somewhat different He dwells quite extensively on the importance of hydrogen-ion concentration in colloidal work, especially in the case of the proteins

Hydrogen-ion concentration, however, seems to be of equal consequence in work on emulsions and colloidal dispersions of all sorts. As an illustration of this point, in the case of oil-in-water emulsions, which all carry negative charges, it is obvious that for the sake of stability it is advisable to have an excess of hydroxyl ions present. If there is an excess of hydrogen ions, a great amount of the effect of stability is offset due to the neutralizing of the negative charges on the dispersed particle, hence approaching the isoelectric point and the zone of unstable equilibrium.

A great number of people are today operating chemical plants involving colloidal problems, who apparently have not realized the importance of hydrogen-ion concentration in relation to their own case In one recent incident, in which the author was consulted, the manufacturer had considerable difficulty controlling his product properly. He was dispersing a material which was of a strictly colloidal nature. In the preparation of this product it was necessary to get peptization at a certain point in order to obtain a complete breakdown This dispersion was being accomplished by the use of a colloid mill. It was found that

[3] Loeb, *J. Gen Physiol.,* 1, 39, 237, 353 (1918) , 2, 459, 483 (1919).

on some days the product went through the process very successfully, whereas in other instances the entire product was spoiled. They were not able to determine just what the trouble was. Needless to say, upon investigation it was quite obvious that it was largely a question of necessity for hydrogen-ion control. The colloidal material was treated in alkali and afterwards flocculated in acids, with varying concentrations, time of exposure and temperature of treatment. As these are all factors in chemical actions it was, of course, very necessary to standardize them. The problem was how to accomplish this so as to obtain consistent results. This again led back to hydrogen-ion control. It was easy to govern the time of exposure and the temperature, but the question was how to get the same chemical activity in that period of time. As the chemical activity was entirely governed in one stage of the process by the amount of hydroxyl ions present, and in another stage of the process by the amount of hydrogen ions present; or, in other words, the true chemical strength of the acid and alkalies used, the only way that this could be done was with hydrogen-ion control. In this particular process there was, undoubtedly, a great amount of adsorption taking place, but the concentration of the ions was the important factor. It meant either the success or failure of the entire process, on which a large amount of money had been spent in development. From this illustration, the reader will readily appreciate that the question of hydrogen-ion control is a vital factor in a great number of instances in colloidal dispersions, from emulsions to and including the dispersion of solids in liquids. In each case the question of electrical charges is encountered, and in questions of stability, this involves hydrogen-ion control.

METHODS OF HYDROGEN-ION CONTROL

The complicated methods of determining hydrogen-ion concentration have held back its popular application for quite a few years. While a great number of concerns have adopted the method of electrical measurements, the determination has been a handicap to others, due to the expense involved in equipment, the time consumed in making the test, and the idea which has prevailed that they must have a trained chemist for making these determinations. In order to simplify this operation various colorimetric methods have been devised, some of them being very highly successful. Some of these, on the other hand, have met with objections in the case of turbid solutions. The colorimetric methods seem to have been objectionable in all practice in the application of colloidal problems, for they were not accurate with the turbid solutions which usually occur in such work. There has, therefore, been a long-felt need for some simple type of equipment to make such determinations with accuracy. Eliminating the above-cited objections and

also being available for field work, such equipment must not involve deli-
cate apparatus, and should be easily handled by anyone. It was desired
to improve the method so that it could be used in practical commercial
operations and not be confined too much to research laboratories. With
this in mind, the author has adapted a new type of set, which seems to
be very satisfactory in practical work. It is very simple to operate and
one that can be put in the hands of plant superintendents and foremen
for pH control without their having to know anything about the theory
after the standardization on the process has once been made. The
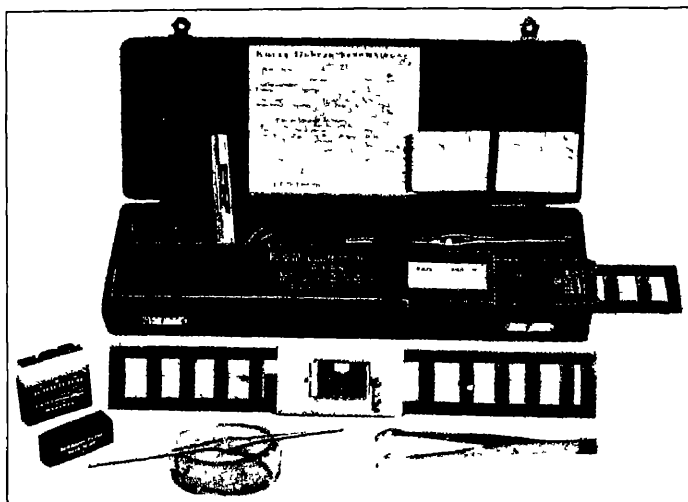
FIG. 4.—Hydrogen-Ion Set for pH Control.

accuracy of the determinations by this method in field work seems to be
within a pH value of 0 10, which for all practical colloidal applications
is ample While the work on this set has proven of no great advantage
in clear solutions, it has been found a great convenience for work on
emulsions and turbid solutions in general; also of great advantage in
simplicity of operation and speed of determination. Through this it
has been possible to help a great deal in placing various colloidal prob-
lems about the plant on a basis for hydrogen-ion control. This, after
all, is the main object in getting proper conditions. Without plant con-
trol, most colloidal processes would be failures. Of course hydrogen-
ion control is not everything but it is an important consideration of all
dispersions of solids into liquids, and in general emulsification work
It is, of course, also a factor in connection with filtration problems, and
it is believed that with proper hydrogen-ion control a great number
of colloidal problems will be simplified greatly and more uniform
results will be accomplished in the future.

Chapter VIII.

Orientation.

While the orientation theory has been mentioned from time to time, and discussed briefly in the chapter on emulsification, it is necessary to go more in detail into this theory so that one may visualize the state or structure in which the film at the interface is supposed to exist In view of the importance of orientation in the study of all dispersions, it is advisable to devote a brief chapter to this subject alone.

While, in some instances, it is known that the film in the interface is more than a molecule thick, yet in some of the most stable emulsions the emulsifying agent is present only in traces, and due to the concentration of the dispersed phase it could not be present in sufficient quantity to protect such phase with much more than a molecular coating. As an example of this take an emulsion which occurs in nature, rubber latex, which contains approximately one-third of the dispersed phase. The emulsifying agent is apparently present in such small quantities that it has been difficult to determine just what is present which causes the emulsification; yet latex is a very stable emulsion when first recovered from the rubber plant. While ammonia is usually added to this product to prolong its period of stability, this merely increases the hydroxyl ions, enabling the particles to maintain their proper difference in potential and offset the effect of the electrolytes in the air and thus avoid flocculation.

VALENCY FORCES AND MOLECULAR FILMS

While forces at the boundary between the dispersed phase and the liquid in which it is dispersed depend a great deal upon the difference in potential and other physical conditions, Langmuir[1] and Harkins[2] have come to the conclusion that these forces are largely chemical When one makes an investigation of the nature of the forces which keep the dispersed particles in suspension, it is immediately realized that a stabilizer of some sort must, as a rule, be present. These stabilizers are very frequently emulsoids, of which gelatin is a typical example, but in the case of other dispersion agents, such as

[1] Langmuir, *J. Am. Chem Soc*, **39**, 1848 (1917)
[2] Harkins, Brown and Davies, *J. Am. Chem Soc*, **39**, 354 (1917)

soap, sulfonated oils, etc , it is necessary to discriminate between the "aqueous groups" which have a strong chemical affinity for the water molecules. Such aqueous groups are the carboxyl in the case of soaps and the amino in the case of proteins Then there are the hydrocarbon groups, which may be spoken of as "oily groups." These have a stronger affinity for each other than for the water. Now, the forces which keep crystalloids in solution are, according to Langmuir, Harkins and other investigators of the orientation theory, forces of secondary valency The attraction between certain groups of the molecules of the solute and those of water is what carries these products into solution

In order to clarify this matter reference is made to the work of Langmuir.[3] He points out that acetic acid is readily soluble in water, for the reason that the carboxyl group (COOH) has strong secondary valency by which it combines with the water. Oleic acid, on the other hand, is not soluble because the affinity of the hydrocarbon chains for the water is less than their affinity for each other. Therefore, "when the oleic acid is placed on the water it spreads, for by so doing the carboxyl group can dissolve on the surface of the water without separating the hydrocarbon chains from each other " If this surface is sufficiently large so that the acid may spread out, the double bond of the hydrocarbon chain is drawn on to the surface of the water, and in such event, the area occupied is far greater than in the case of a saturated fatty acid. Pure paraffin oil (which does not contain such active groups, in other words is a straight hydrocarbon) will not spread on the surface of the water to the extent of oleic acid, for it does not contain a group with affinity for water; that is, it consists entirely of what may be considered as "oily groups." Oleic acid in contact with a large quantity of water will spread until it forms a layer one molecule thick and will be oriented in relation to the water. It will spread upon the surface so that each carboxyl group is in contact or combined with the water, while the hydrocarbon groups are placed side by side vertically above the carboxyl groups, in other words, the surface of oil film consists of the CH_3 groups.[4] Due to this orientation there should not be any tendency for another layer of oil molecules to spread on top of the first. If the upper group consists exclusively of CH_3 or other hydrocarbon groups, there is no secondary valency and no particular attraction for the second layer, while in globules of oleic acid the carboxyl groups are distributed in all sorts of ways throughout the mass. "It would be more natural for them to take this position than to spread out in layers two molecules deep." [5]

[3] Langmuir, *loc cit* , p 1850.
[4] Langmuir, *loc. cit.*, p. 1848
[5] Bancroft, "Applied Colloid Chemistry," 2nd ed , McGraw-Hill Book Co , New York, 1926, p 99

The spreading qualities of oleic acid, when given sufficient space on water, present a strong evidence in favor of the orientation theory. Harkins[6] and Adams[7] state that when the area over which the oil drops spread is reduced, the film will remain one molecule thick as long as there is sufficient surface for this spreading When the surface is decreased beyond this point, the film buckles and goes into the form of globules and not a single case out of several thousand experiments could be found where the molecules were two or more deep in the surface layer.

In proteins we have groups which have greater affinity for water than for each other, or the "aqueous groups," and those which have a greater affinity for each other than for water, or the "oily groups." As stated by Loeb,[8] "if the forces of the aqueous groups prevail, the oily groups may be dragged into the water. With large molecules and when the oily groups are scarce, it may happen that the oily groups of two adjoining molecules come in contact These may adhere without noticeably diminishing the forces with which the aqueous groups are held in the water."

FURTHER EVIDENCE OF ORIENTATION

As further evidence in favor of the orientation theory, Hardy[9] brings out the point that lubrication depends largely upon the adsorbed films. While the principle of lubrication is to decrease friction by forming a film between the moving parts to keep the two solid faces from cohering, the better lubricant is more strongly adsorbed on the face of the solid. Bancroft[10] points out that the olefines are better lubricants than the paraffins and that "a systematic orientation of the adsorbed molecules seems desirable." It seems probable that the hydrocarbon or oily groups of fatty acids are in contact with the metal surface and that the carboxyl groups are away from such surface Thus, with a chain hydrocarbon such as a paraffin, the minimum friction is reached almost at once, "for it makes very little difference which end of the carbon chain is attached to the metal." On the other hand, an appreciable time is perhaps necessary before the molecules of fatty acids are oriented in the same way and in such a manner that the hydrocarbon or oily groups are in contact with the metal.

The Helmholtz[11] theory of cataphoretic migration assumes that

[6] Harkins, *J. Am. Chem. Soc*, **39**, 354 (1917); **43**, 35 (1921).
[7] Adams, *J Phys Chem.*, **29**, 87 (1925).
[8] Loeb, "Proteins and the Theory of Colloidal Behavior," 2nd ed, McGraw-Hill Book Co, New York, 1924, p 101.
[9] Hardy, "Fourth Report on Colloid Chemistry," p. 785 (1922); *also see* Hardy and Doubleday, *Proc. Roy. Soc.*, **100A**, 561 (1922).
[10] Bancroft, *op. cit*, p 83
[11] Helmholtz, *Wied. Ann.*, **7**, 337 (1879).

the sign of migration is determined by a film of water which adheres to and moves with the dispersed particles This film is usually negative in its charge, due to an excess of negative ions which are forced into the film through forces present in the water (presumably surface tension). If the two ions of an electrolyte lower the surface tension of the water to a different extent, that ion which has the greater depressing effect on the surface energy tends to concentrate in the outer layer; that is, the stratum which adheres to and moves with the particle It may be that the molecules of water are oriented by such forces at the surface of the water, in which event the hydroxyl ion forms the outermost and the hydrogen ion the deeper stratum of the surface.[12] Therefore, negative ions are forced in excess into the outermost stratum at the surface of the water and the positive ions are in excess in the stratum beneath. This gives a condition similar to an electrical condenser.

All of these facts agree with the idea that the cataphoretic migration is dependent upon the potential difference of the electrical double layer; that this is determined, at least partly, through the forces inherent in the water; and that the influence of electrolytes is practically the same if the particles be coated with gelatin or crystalline egg albumin. This influence on the suspension of the particles is entirely different if the egg albumin has been denatured. This difference is probably due to the fact that the forces determining the stability of the suspensions of gelatin-coated particles in water are the strong chemical forces acting in true solubility. On the other hand, with the denatured albumin the suspension of the particle is merely dependent upon the weak electrostatic forces of the double electrical layer surrounding the particle [13] The egg albumin exists in two modifications, genuine and denatured The genuine crystalline egg albumin is highly soluble in water; that is, peptized by water. The denatured albumin is practically insoluble. The change in the albumin can be brought about by merely heating above the critical point while in water solution According to Loeb, the forces which keep genuine egg albumin in solution are the strong secondary valency forces, while the forces which keep denatured egg albumin in solution or suspension are merely the weak electrostatic forces of repulsion, due to the Helmholtz effect This supports the idea that the genuine egg albumin, when it forms a film over the dispersed particle, must have these forces of secondary valency. When it is heated the orientation is in some manner changed and the groups which had the affinity for the water have been either

[12] McTaggert, *Phil. Mag ,* **27,** 297 (1914) , **28,** 367 (1914).
[13] Loeb, "Proteins and the Theory of Colloidal Behavior," 2nd ed , McGraw-Hill Book Co, New York, **1924,** p. 338.

destroyed or modified and the egg albumin is no longer of much benefit as a protective colloid.

DENATURING EFFECT OF DRY GRINDING OR HEATING

Herzfeld and Klinger [14] found that straight mechanical grinding of blood albumin to the form of a dry powder will render such albumin insoluble   The denaturing effect on albumin is very interesting and has also been the cause of some controversy, especially in connection with the making of mayonnaise dressing   Many mayonnaise manufacturers have tried to make this dressing by passing the entire product through a so-called colloid mill, or homogenizer, which invariably causes a curdling action   Apparently the albumin is denatured by such treatment and the entire emulsion breaks if the product is treated with any amount of pressure, high-speed agitation or shearing action brought about in a colloid mill. Apparently the denaturing effect upon albumin can also be brought about when the product is in the presence of liquids, providing the mechanical treatment is sufficiently vigorous 'The mechanism of denaturing is unknown but it is possible that the albumin molecules of the film are oriented and that through heating or other means the groups with the water affinity are rendered ineffective   A thorough study of this condition would be of great benefit to the mayonnaise manufacturer and would be of considerable assistance in the making of stable dressings

ORIENTATION IN DISPERSION

The observations of Langmuir, as well as of numerous other coworkers leave very little doubt that the molecules of surface films, at least in a great number of cases, are definitely oriented   Most workers have now abandoned the idea, which existed over a great period of years, that the molecules were perfect spheres. We are beginning to realize that they undoubtedly have a definite structure. The idea of molecular orientation not only seems very plausible but there is strong evidence that it occurs, and this in turn is a great factor on some of the physical observations on surface films. Time will probably prove that there is a very close connection between certain physical characteristics and this secondary valency   It at least gives us some explanation of the peculiar results occasionally encountered in dispersions.

[14] Herzfeld and Klinger, *Biochem Z.*, **78**, 349 (1917)

Chapter IX.

Gel Structure and the Donnan Theory of Membrane Equilibrium.

When a substance is insoluble in a solution, or conditions are changed so as to decrease the solubility, a precipitate is formed. This may be crystalline or in the so-called amorphous state, dependent largely upon the conditions under which the precipitate is formed. If the precipitated substance holds any quantity of liquid within the mass, it will form what we call a gel or gelatinous precipitate. If such gel formation holds all the liquid at first, then, and under such conditions, we frequently speak of it as a jelly If, however, surplus liquid separates therefrom, we usually refer to it as a gel This distinction between the two types of precipitate is rather arbitrary. The jelly is more rigid than the gelatinous precipitate or gel. However, they are all gels, and are spoken of as "gel structure" which takes in the entire group

The colloidal condition known as the gel is easy to recognize but rather difficult to define, as it is confused by the fact that the limits between gel and sol, and the gel and what may. be termed the curd, are not precise. The one seems to overlap the other, and there is a gradual change from one state to the other. Thus, throughout the literature one finds a confusion as to gels and jelly. There is one rule, however, which holds for all gels, and that is, they must be built up of two components. One is a liquid at the temperature under consideration, and the other, which is the gelling substance, is sometimes spoken of as the gelator, this being a solid. The jelly itself, after it is formed, has the mechanical properties of a solid; for instance, it maintains its form under the stress of its own weight and under mechanical stresses it shows the phenomena of strain. It differs, however, from a solid in other respects, of which the most outstanding is that many substances which are soluble in the liquid component can diffuse through the jelly with a velocity little different from that in the solvent. Another outstanding difference is that chemical reactions can occur in jelly almost as rapidly as in a liquid A gel shows the Tyndall effect and yet is transparent to the eye.

VARIOUS GEL STRUCTURES

Some distinction must be made between true gels, such as occur in agar, soaps, gelatin, etc., in which the interlocking fibers must adsorb much water, and the false gels of the caffein type, in which the interlocking needle-like crystals entangle considerable water without actually adsorbing it on the surface of the crystals Between these two extreme cases there must be various gel structures The ease with which diffusion takes place through gel structure indicates some sort of continuous channels for the solution. Whether the structure of the gel formation is of the honeycomb type or is a series of filaments, or brush-heap structure, is not yet positively known. It is obvious, however, that it is a solution containing some sort of network or cell walls enclosing the dilute solution, and that such solution must be connected throughout the mass, so as to give rapid diffusion.

It is evident that the setting or solidification of sols of gelatin agar, etc., forming solid jellies on cooling, is considerably different from the ordinary precipitation or coagulation. Also, it is evident that these gel formations vary greatly in concentration with different materials, for a 1 per cent gelatin will form a light gel structure, while an equal amount of agar-agar forms a hard gel. There may be a gelatinous precipitate with a supernatant liquid, or the whole mass may set to a solid gel, and the jelly may afterwards contract or squeeze out some of the surplus liquid. Where this occurs it is spoken of as syneresis. The term jelly is generally understood as the solid formation of gel structure where there is no surplus liquid, for we speak of a gelatin solution setting to a jelly. The term gel includes the entire group of gelatinous precipitates, jellies, etc. Hence, the term gel covers the entire series of gelatinous precipitates and formation of jellies, and really applies to the structure rather than to the special forms which occur.

INVESTIGATIONS OF CONSTITUTIONAL STRUCTURE

One of the great handicaps in the investigation of gel structure has been that the gelatin gel, for instance, appears perfectly clear and homogeneous to the eye, and even under the highest powers of the microscope no structure is revealed Even with the ultramicroscope no individual particles are disclosed, yet the Tyndall effect indicates a fine-grained structure. General acceptance of these substances as typical of the colloidal state has necessitated detailed investigation of their properties, in spite of the fact that their constitutional structure still remains undisclosed. Perhaps one of the greatest handicaps to date in investigating gel structure has been the tendency to regard

colloidal substances as having properties altogether peculiar in themselves rather than regarding such substances as in a particular state of matter. In the case of gels the question is, how is this water held in a solid form and what is the constitution of the gel? Much progress has been made in the past few years, however, by investigating gel structure with the thought constantly in mind that it is some sort of a honeycomb or brush formation and that the liquid phase is in contact throughout; also that these filaments, or the brush formation, must be all interlocked or connected together throughout the mass and that the water or other solution in the gel must be held by adsorption. While there is no difficulty in recognizing gel structure, there has been great confusion as to just what sort of structure is built up around the water phase.

In building up, gel structure is always viscous and contains adsorbed liquid. This is the so-called colloidal viscosity and borders very closely on a plastic condition, and certainly becomes decidedly plastic when approaching the condition of jelly. If a very finely divided solid adsorbs water to a great extent, it will, of course, become gelatinous Very fine crystals, which have a high degree of water adsorption, are frequently referred to as gelatinous materials and are usually fine needle-shaped masses which are very thin and flexible and can be bent and twisted into various shapes. These fine crystals will build up a gelatinous structure when they are in clusters, forming a network, and in the presence of excess water form a gelatinous precipitate.[1] If the crystals are rigid, they will not necessarily form a gelatinous precipitate, unless they united into threads or strings so as to have flexibility. In a gelatinous precipitate, which is supposedly a network composed of extremely finely divided particles which form filaments or chains, the particles must be highly hydrous. If they do not have any great amount of water adsorbed on their surfaces and little tendency to coalesce and form filaments of threads, a high concentration is necessary in order to have proper water adsorption to give the precipitate a gelatinous character. Very frequently in dispersion of mineral matter, such as fine calcium carbonate or magnesium hydroxide in the making of milk of magnesia, a gelatinous precipitate is present, and if sufficiently concentrated, gel structure is obtained. Of course, in such cases, the concentration must be sufficient to obtain a fairly high degree of water adsorption.

Frequently, in colloidal dispersion, it is noticed that the material goes into the so-called colloid mill quite thin but is discharged from these mills in a thick condition, with more or less of a gel structure, and the material is really plastic. This is always a pleasing indication

[1] Bancroft, "Applied Colloid Chemistry," 2nd ed, McGraw-Hill Book Co, New York, 1926, p. 318.

to the operator of the machine and is usually attributed to fine dispersion, which is partially true. Nevertheless, the product must be in condition to have proper water adsorption or one would not get this gelatinous appearance.

VARIOUS THEORIES OF GEL STRUCTURE

From what has previously been discussed, one will readily appreciate that a gel may have a structure varying from a granular mass and interlocking threads on through to a honeycomb structure This takes us from the extremes of gelatin in the form of jelly on through to fine dispersion of pigments, all being classified as gel structure. It is believed, for instance, in the case of a soap solution (when it sets to a gel) that long threads are formed and these may be carried on over to a net structure. We have, therefore, up to the present, no definite theory which applies to all gel structures. The gel may be composed of long strings of molecules or continuous crystals irregularly deposited, forming a network. Many theories have been proposed and they may be classified into groups One class embraces those in which there are two phases, a liquid and a solid To this class belongs Procter's hypothesis [2] that jelly is a. solid solution of a liquid in the colloid substance, also McBain's views [3] that identical colloidal particles are present in the sol or gel state and they differ in mechanical properties only.[4] There are numerous other theories on gel structure and among them is one of the older ones, that a gel has a solid phase composed of molecular complexes or micelles with crystalline properties and that the water is held by molecular attraction. A modification of this hypothesis popular at the present time is that the water is held by adsorption throughout the filament. Bradford [5] believes that a gelatin jelly is crystalline. Moeller [6] believes that the gel structure is due to a lattice of crystal threads which entrains the liquid. In any event, there must be some sort of solid network throughout the system and the liquid phase must be connected throughout so as to get diffusion.

PROPERTIES OF GEL STRUCTURES

Jellies form from colloidal solutions if there is a sufficient amount precipitated at proper rate and without agitation.[7] If the concen-

[2] Procter, *J Chem. Soc*, 105, 313 (1914)
[3] McBain, *J. Chem. Soc.*, 117, 1506 (1920)
[4] Bradford, in Alexander's "Colloid Chemistry," Vol 1, Chemical Catalog Co, New York, 1926, p 751
[5] Flade, *Z. anorg. Chem*, 82, 173 (1913)
[6] Moeller, *Kolloid-Z*, 23, 11 (1918)
[7] Holmes and Fall, *J. Am. Chem. Soc*, 41, 763 (1919).

tration is low, the jelly does not form, or only a soft jelly is formed. If the precipitation is too rapid, contraction is liable to occur, bringing about syneresis, or even resulting in a gelatinous precipitate instead of the formation of solid jelly. If the precipitation takes place slowly and separates out uniformly, a jelly is obtained, if sufficiently concentrated, but this may afterwards contract and squeeze out liquid. If the gel structure is not too rigid, or in other words, if a light gel is obtained after cooling, this may be agitated and the gel structure broken. This liquid may remain fluid thereafter, if not re-heated. This is the basis of some processes that the author has used quite extensively in the making of certain emulsions, where a decided gel formation takes place after the product is cooled in the storage tank. This is agitated after slow cooling and the gel structure destroyed sufficiently so that the emulsion can be bottled. It is very important in the manufacture of this emulsion that the product be allowed to cool slowly and then agitated. This is the popular way of making a modern so-called mineral-oil agar emulsion. There is just sufficient agar in it to cause a light gel formation after homogenizing. This gel structure is broken after the product is cooled. It will not re-form as long as the finished product is not re-heated. The gel structure may re-form on heating; but, in such instances, a slight shaking of the product will again make it fluid. This apparently is merely the breaking down of the gel filament or gel structure.

The properties of jellies are effected by the presence of tough skins formed on the surface after evaporation of some of the liquid phase, these particles then become cemented together. In the case of a solid gel this skin is very noticeable, especially after being exposed to the air for several days. When carefully heated so as not to melt, the skin cylinders of such gel formations expand in the direction of their greatest length, due to the restriction of expansion imposed by the skin.[8] With skin formation on gelatin jellies, this is quite noticeable, with agar jellies it is much less so. Nevertheless, this skin formation might occur on any jelly due to evaporation at the surface. In agar jellies a noticeable gel formation commences at 0.4 per cent, and a 1 per cent agar jelly is about as stiff as an 8 per cent gelatin jelly.

An interesting case of gel formation is that of the soap jelly. It may be clear, transparent and an elastic gel, and the conductivity is not diminished. "The only difference, in fact, between the sol and the gel appears to be the mechanical rigidity and the elasticity of the jelly. Neither type, that is, the sol or the gel, shows any structure in the ultramicroscope."[9] This indicates that the soap jelly is the same as that of the soap sol, but that the suspended particles in the gel, which

[8] Bradford, *op cit*, p. 765.
[9] Bancroft, *op. cit.*, p 324

might be filaments, adhere to one another sufficiently to give an elastic jelly.

It has been noted that a silica gel containing a great deal of water shrinks very much when this water is removed, but upon the addition of water the volume change is not reversible. A gelatin jelly can be reversed if additional water is added, for if dry gelatin is placed in cold water it takes up more than ten times its weight of water. Of course, to form the jelly it must be heated. This apparently indicates that the structure of gelatin has an important bearing on the rate of swelling "If a silicic acid gel is heated it sinters and contracts, making the pores finer," [10] therefore, they do not hold so much water. This structure evidently does not go back again to its former state, while a gelatin jelly has a tendency to do so.

To sum up the question of gel formation in brief form, a gel is a system which possesses mechanical rigidity and yet allows diffusion to take place in its mass at somewhat similar rate to that in liquids Gels must consist of two components, a liquid solvent and a solid solute. Again, gels are only formed from super-saturated solutions An emulsion of two liquids may be made to simulate a gel if a third component which forms a continuous solid film at the interface is introduced. This structure must have in some instances a similar condition to that which we observe in emulsification.

The Donnan Theory of Membrane Equilibrium

The effect of the presence of salts on jelly formation is determined to a great extent by the precipitating and stabilizing action of the ions in so far as they effect the rate of precipitation, and there is little doubt but that the Donnan theory of membrane equilibrium should be given serious consideration when one is studying gel structure It at least is of great assistance in visualizing what occurs in the case of the swelling action in gel formations.

Osmosis as Applied to Gel Structure

Before going into details regarding the Donnan theory of membrane equilibrium, however, it is desirable that we again touch on the subject of osmosis. This can be well illustrated with a sugar solution If one takes a solution of sugar and pours it into a parchment sack or other organic membrane, then in turn places water on the outside of such membrane, the water will diffuse through with a tendency to dilute the sugar solution. It will continue until the pressure in the membrane offsets the pressure of the water flow into

[10] Bancroft, *op. cit.,* p 333.

the sugar solution, that is, until the diffusion has proceeded as far as possible so as to equalize the pressures on both sides of the membrane. The rate of diffusion is inversely proportional to the mass or weight of the molecules, hence its value in determining molecular weights. In comparison with the weight of the sugar molecules, the molecular weight of water is small. The water passes through the membrane by osmosis and a pressure is set up on one side of the membrane. If the membrane is enclosed, the pressure can be measured with a mercury gauge. If substances in the colloidal state are in dispersion in the membrane, the diffusion is so slight that no osmotic pressure can be detected

If an electrolyte, such as sodium chloride, were present inside the membrane, a false pressure reading would be obtained, for there would be dissociation of the electrolyte into its ions and the tendency for it to dissociate further on dilution Thus, the pressure readings would be made much higher. The general rule on molecular weights, therefore, does not apply with an electrolyte. True molecular dispersion is obtained in the case of a sugar which does not dissociate into ions.

By means of the Donnan theory of membrane equilibrium Procter [11] and Wilson [12] explained the increased swelling action of gelatin in dilute acids and alkalies While gelatin may not actually combine with the acids, the evidence points that way. On this theory of osmotic pressure bringing about swelling action in gelatin and other colloids, it is believed that as soon as the osmotic forces are greater than the cohesion between the particles peptization takes place. In order that the reader may have a clear conception of the swelling action in gel formation, some of these points will be illustrated in the case of gelatin, and references will frequently be made to the work of Loeb.[13]

THE SWELLING ACTION OF GELS

The theory on such swelling action consists briefly in that hydrochloric acid when first added to gelatin forms a gelatin chloride which dissociates electrolytically The gelatin ion cannot diffuse out from the jelly, while such jelly is easily permeable to the ions of the acid. In consequence, a membrane equilibrium is set up between the liquid inside of the jelly and the solution outside, whereby the concentration of the colloidal ions is greater inside. This brings about excess of osmotic pressure of the solution of crystalloids inside the jelly over that in the outside solution, and leads to diffusion of water into the gel,

[11] Procter, *J. Chem. Soc.,* **105,** 313 (1914)
[12] Wilson, *J Am Chem. Soc,* **40,** 886 (1918)
[13] Loeb, "Proteins and the Theory of Colloidal Behavior," 2nd ed., McGraw-Hill Book Co., New York, **1924,** p. 358.

which causes its swelling. This swelling action is limited to the force of cohesion between the molecules of the jelly or gelatin and when one goes beyond this point, peptization follows.

According to the work of Procter, the gelatin ions constitute a jelly of gelatin chloride which cannot diffuse, hence, not exercise osmotic pressure. This is true so far as the gelatin portion of the combination is concerned, but the chlorine anions in combination with them, or retained by the jelly, exert osmotic pressure by electrostatic attraction This difference in the diffusibility of the two opposite ions of gelatin chloride gives rise to the Donnan membrane equilibrium. To demonstrate these points, Procter put solid gelatin chloride into an aqueous solution of hydrochloric acid and determined by titration and distribution of free hydrochloric acid inside the gel and also outside at the time of equilibrium. From this Loeb [14] derived a mathematical and quantitative explanation of the influence of electrolytes on colloidal behavior of a protein solution

The condition for establishing the membrane potential is explained by the existence of a block to the diffusion of one type of ions, which are those combined with the gelatin, while no such block exists for the crystalloidal ions or those not in combination with the gelatin. Hence, when the acid is added to solid isoelectric gelatin, it is ionized in the same way as if it were in solution, for we know that we can get diffusion through gelatin the same as in solutions. This block which prevents the diffusion of gelatin ions consists of the forces of cohesion between certain oily groups of the gelatin molecules or ions and gives rise to this difference in membrane equilibrium. This leads to increase in osmotic pressure and to the establishment of a potential difference between the jelly and the solution surrounding it One should note that if a potential difference is created in this manner, as described by Procter and Wilson [15] and given more in detail by Loeb,[16] when an emulsion is formed, there is, as a rule, an organic membrane surrounding the oil globules. In this case also a potential difference can be obtained which is usually attributed to the adsorption of the ions on the surface of the micelle. There is a possibility that with further study of the cause of the swelling action in gelatin a real clue may be obtained as to the difference in potential and the reason for the adsorption of the ions on the surface of such dispersed particles

BLOCKING THE PROTEINS

It is certainly justifiable to consider proteins as crystalloids which show colloidal behavior only under certain well-defined conditions,

[14] Loeb, *op cit*, p. 28, 70
[15] Procter and Wilson, *J. Chem Soc.*, 109, 307 (1916).
[16] Loeb, *op. cit.*, p 240, 241

for example, when there exists a block to the diffusion of the large protein ions but not a diffusion of the smaller crystalloidal ions. This block may be produced by a great number of membranes which are impermeable to protein ions in so-called solution but permit the crystalloidal ions to pass through. This difference in the molecular concentration of the crystalloidal ions on the inside and outside of the protein membrane or gel structure may give rise to the colloidal behavior, making the difference which is noted in such instances.

The differences between colloidal behavior and crystalloids, as pointed out by Loeb, are as follows· the difference in membrane potential in the case of colloids, the difference in osmotic pressure, colloids not exhibiting this property but showing a swelling action when electrolytes are added, and the difference in the form of viscosity, crystalloids giving what we would call true viscosity, while colloids give a form of viscosity all their own. This is due to the swelling of submicroscopic particles in the jelly, as inferred by Loeb,[17] explained by the Donnan theory. The colloidal behavior is restricted to the conditions where the diffusion of one ion is prevented while no such block exists for the diffusion of the other ions. According to this viewpoint "if we were in a position to produce membranes impermeable to calcium but permeable to chlorine or sodium ions, solutions containing calcium chloride and sodium chloride would show colloidal behavior" in respect to the influence of· electrolytes on membrane potentials as well as osmotic pressure, viscosity, etc

In colloidal behavior "the reason for osmotic pressure, viscosity and the swelling of protein gels all being influenced in a similar way by electrolytes is that all these properties are, in the last analysis, functions of one and the same property, that is, osmotic pressure." Loeb[18] goes on to show that the viscosity of protein solutions is affected by electrolytes in a way similar to their osmotic pressure. Also, that this swelling is due to osmotic pressure inside the aggregates, and is brought about when the protein ions are prevented from diffusing, while the smaller ions of the crystalloids can diffuse through such membranes. The colloidal properties of such proteins, swelling action, osmotic pressure, viscosity, etc, show a minimum of their values at the isoelectric point; probably because the ionization of proteins is a minimum at that point.

CONCLUSIONS

Loeb has gone very extensively into this work, and the present author merely desires to point out a few of the important relations

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[17] Loeb, *op cit.*, p. 368, 369
[18] Loeb, *op cit*, p 32, 36.

so as to assist, if possible, in giving a clearer vision on the swelling action and other colloidal properties. The evidence is quite strong in showing that the osmotic pressure and swelling action of gelatin, as well as the so-called colloidal viscosity, are all related. They, at least to a great extent, depend upon the Donnan theory. One might put these facts together and arrive at the conclusion that the action of salts on the stability of gelatin solutions supports the idea that gelatin forms crystalloidal solutions as do also other proteins, such as crystalline egg albumin. These proteins have a minimum of solubility at their isoelectric point and the solubility increases with its degree of electrolytic dissociation. The valence of the ion with which a protein is in combination determines its osmotic pressure rather than the chemical nature of the ion. This, of course, comes back to the dependence upon the electrical charges carried by the ions.

From the evidence presented by Loeb, as well as by Procter and Wilson, accounting quantitatively for the process of swelling in gel formation, the Donnan theory of membrane equilibrium gives at least a plausible explanation. The force which opposes and limits the swelling is the cohesion between the molecules or ions constituting the gel, and when such force is diminished, the swelling should increase. Procter and Wilson point out that this is the case, for the swelling of the gelatin increases when the gel is heated. The establishment of Donnan equilibrium is only possible, however, when the protein is ionized and the diffusion of protein ions is prevented without interfering with the diffusion of the other ions present in the solution. While it is true that Loeb's work was all conducted within narrow limits, nevertheless it has brought about a new interest in the theory of Donnan. How far this can be carried in the applications of other types of colloids it is difficult to say, for most of the work along this line seems to have been carried on with gelatin. Stiasny and Ackermann [19] observed, however, that the dry powders of skins swell more in high concentration of salts or electrolytes than they do in water. This may be brought about by an increase in the solubility and a decrease in the cohesion between the molecules of the solid collagen whereby the water is able to diffuse into the otherwise impermeable membrane.

[19] Stiasny and Ackermann, *Kolloidchem. Beihefte,* 17, 219 (1923).

Chapter X.

The Protective Action of Colloids in Dispersions.

The principle of protection against flocculation by the use of colloids in dispersions is not new. In fact, it goes back to ancient times, and was apparently practiced in the early days by the Chinese in making India ink by deflocculating lampblack by the use of a glue. The ancient Egyptians used gums in their inks so as to avoid flocculation, and also prepared their clays by the use of colloidal materials, making them plastic so that they were workable. The Babylonians used infusions of straw for making their clays plastic.[1] Hence, while such principles may not have been understood at the time, it was common knowledge that better results were accomplished by the addition of emulsifying agents or stabilizers to protect the dispersed particles

A protective colloid or stabilizing substance is one which opposes the aggregation or flocculation of particles into larger groups. Generally speaking, the so-called emulsoid colloids, such as gelatin, albumin, soap, gum acacia, etc., act as protectors in water dispersions.

While most colloidal dispersions depend, for their stability, on the presence of protective colloids, they are not necessarily of the emulsoid group. We may use such colloidal substances as zinc and magnesium resinates, which are insoluble in the water phase but can be dissolved in oil, as protective colloids or stabilizers for pigments, and thus form dispersions. These principles can be used in light naphthas and other solvents. There are other cases, such as the dispersion of zinc oxide into oil for the making of white paints, where the material is sufficiently viscous so that once the product is dispersed therein, flocculation does not readily occur. A slight addition of a protective agent is of great assistance, even in such instances, and will assist in avoiding settling, etc.

Gold Sols

Zsigmondy [2] has demonstrated that stable though highly sensitive gold sols may be made without the use of a protective colloid, provided

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[1] Alexander, "Colloid Chemistry," Vol. 1, Chemical Catalog Co, New York, 1926, p. 620.
[2] Zsigmondy, "Kolloidchemie," p. 173, 358 (1918); also *Z. anal. Chem.,* **40**, 697 (1901).

electrolytes or other coagulating substances are not present. These sensitive sols, however, can be greatly stabilized by the addition of protective colloids. The early experiments of Zsigmondy brought forth the importance of the use of such protective principles and showed that suspensions of colloidal gold might be precipitated by low concentration of salts or other electrolytes, but were protected against such action when the gold particles were suspended in a gelatin solution. Zsigmondy and his co-workers established what was known as the "gold number" and defined this as the number of milligrams of protective colloid required just to prevent a definite degree of agglutination of the gold particles. In order to standardize, a 10 per cent solution of sodium chloride was used, and the gold number was defined as the number of milligrams of protective colloid which would just prevent the flocculation of the gold particles when 1 cc. of the standard sodium chloride solution was added to 10 cc. of the suspended gold particles (0 0055% Gold) Hence by this standardization, the gold number was put on a quantitative basis and has been very valuable for purposes of comparison It is known from the work of Zsigmondy that the protective colloid is adsorbed by the gold particles in suspension and that such particles are surrounded by a layer of gelatin, which acts as the protecting film.

MILK

An excellent illustration of the effect of colloidal protection is that of milk, where the casein, which is an unstable colloid, is protected or stabilized by the lactalbumin. Alexander [3] has shown that cow's milk is much more readily coagulated by an acid or rennin than is mother's milk and that when coagulation takes place in human milk it is of a much finer curd. The addition of any protective agent, such as gelatin or albumin, to cow's milk will make it approach nearer to mother's milk and more digestible when used for infant feeding If the casein is precipitated from cow's milk, it comes down in relatively coarse lumps. The addition of gelatin reduces this precipitate, or at least stops growth into large lumps. In human milk more protective colloid is present and it is found that the balance in such milk is somewhat different from cow's milk. There is more lactalbumin present in mother's milk, hence the finer curd and the reason for it being more digestible.

GELATIN AND ICE CREAM

The property which gelatin, albumin and other emulsoids have of being strongly adsorbed on the surfaces of the dispersed particles and

[3] Alexander, *J. Soc. Chem Ind*, 28, 280 (1909); *also* "Colloid Chemistry," Vol. 1, Chemical Catalog Co., New York, 1926, p 622.

thus keeping down the size of the precipitates, or offsetting condensation, is made use of in the preparation of many colloidal dispersions. The fineness of the precipitate may be largely governed by varying the amount of such stabilizers   One of the common applications of this principle is the addition of gelatin to ice cream, thus preventing the formation of coarse ice crystals in the freezing   This has developed into standard practice to such an extent that there are few manufacturers today who do not use some form of protective colloid The quantity used in ice cream is usually about one-quarter of one per cent of gelatin or its equivalent   This is of great importance in obtaining a smooth product.

Substances such as gelatin, casein, albumin, starch, gum acacia, etc , interfere with the precipitation of insoluble compounds and should be added only in relatively small amounts to give protection in a colloidal suspension   Not only do they protect against flocculation or agglutination, but they also help to withstand the counter-action of the electrolytes up to certain points. This point can be determined by standardizing against a standard solution of an electrolyte in the same manner as Zsigmondy did in the case of the gold number.

PROTEIN COLLOIDS

While gelatin is frequently cited as one of the best types of protective colloids for hydrosols, there are a great number of instances where combinations with protein colloids are more beneficial.   For example, Paal [4] prepared a protective material of about the same power as gelatin by heating albumin with sodium hydroxide, securing what he called "sodium lysalbinate" and also "sodium protalbinate."

The coatings about the dispersed particles are obviously very thin, because there is apparently no diminution in the Brownian movement caused by such protective colloids and, in most cases, very little ultramicroscopic evidence of the existence of the film   From the study of orientation, there is strong evidence that these films are possibly only a molecule thick. It is believed that in the case of a blend of emulsifying agents, the benefit probably comes through what is known as "plural protection," which will be discussed later.

The degree of dispersion is a very important factor in the protection of the dispersed particles, for the protective action is believed to be the adsorption of a layer of the protector at the interface between the dispersed and dispersion medium [5]   The finer the division of the dispersed particles, the more surface area must be covered by the

[4] Holmes, "Laboratory Manual of Colloid Chemistry," Wiley and Co., New York, 1922, p 27.
[5] Bechhold, *Z. phys Chem* , **48**, 385 (1904).

protector. The protective colloids in hydrosols in most instances have considerable attraction for water and a great swelling action. After dissociation, they may swell enough to force the particles far apart and beyond the range of molecular attraction, which is usually estimated to be about 50 $\mu\mu$.[6] In this way, the protective colloid may be of assistance in splitting up the dispersion. It is also realized that, due to the fact that the protective colloids usually have such swelling action, there would naturally be a great increase in viscosity as the amount of dispersion is increased. The emulsoid colloids add considerably to the viscosity of the dispersion medium and are, of course, much less sensitive to electrolytes, as it usually takes a concentrated solution of salts to precipitate them. It is claimed that when such electrolytes do precipitate the product, it is due not so much to the electrical action as to the fact that the colloids are insoluble in concentrated solutions of electrolytes. This, of course, applies only in the case of electrolytes, such as sodium chloride or other salts. In such cases as varying the hydrogen-ion or hydroxyl-ion concentration, there seems very little doubt about neutralizing the electrical charge on the dispersed particle when it has an opposite sign to the acid or basic radical. The addition of an emulsoid colloid to a hydrosol (such as a solution of gelatin to gold) makes it more stable, and also less sensitive to the action of electrolytes. However, the addition of stabilizers beyond the point of · complete protection is of very little additional benefit.

Reversing the Charge

While it is quite evident that oppositely charged colloids precipitate each other by use of an excess of protective colloid, it is possible to offset this action to a great extent. If an excess of a positive emulsoid sol be quickly added to a negative sol, the protector is adsorbed before precipitation occurs and it may be possible to carry a negative sol over to a condition where there is a difference of potential which is positive provided it is carried beyond the isoelectric or neutral point at a rapid rate. If, on the other hand, only a small quantity of the protector is used, or if the protector is added slowly, the precipitation may occur before the difference in potential is reversed. Therefore, precipitation depends upon the speed of mixing of the protective agent as well as the proportions used. Using gelatin as an illustration, if the ratio of such colloid be increased sufficiently, it may pass through the precipitating range to where the dispersoid is stabilized by gelatin, even though the dispersion had an opposite charge. Such dispersion would then act more like a water-soluble colloid. Colloidal gold and silver solutions when stabilized by the use of gelatin may be evaporated

⁶ Alexander, *op. cit.*, p. 621.

and dried and upon the addition of water will again dissolve. The gelatin has coated the particles and prevented the irreversible agglomeration. When too small a quantity of gelatin is used, it may retard but not prevent such agglomeration upon drying.

AUTO-PROTECTION

Every substance, in various degrees of dispersion, from the atomic groups on through to the molecular groups or micelles, which may be large enough to be visible, must at times have particles of colloidal dimensions. Therefore, when a colloidal dispersion of a substance is in contact with larger particles of the same substance, they may be adsorbed and there may be "auto-protection, where the substance delays or prevents its own crystallization"[7] Crystal formation is, perhaps, preceded by tiny globules which may protect and offset crystallization. We have the condition wherein the colloidal dispersion, of the substance is in contact with a non-colloidal phase of the same substance and in that way protects the dispersion from flocculation. The general rule in colloidal protection is that anything which destroys the protector will tend to cause the protected dispersion to coagulate. Anything that protects the protector, that is, assists in making it more stable, will cause the dispersion to be more resistant to coagulation or flocculation. Thus, sometimes a blend of protecting agents is of benefit. In an oil-in-water type of emulsion where the globules carry a negative charge, it is of assistance to add a slight trace of alkali to increase the difference in potential by adsorption of the hydroxyl ion on the surface of the protective colloid and make such product more resistant to coalescence of the oil droplets. The addition of a germicidal agent in cases where casein is used as a protector will offset the bacterial action which otherwise would occur, resulting in the destruction of the casein film. In this way casein can be used as a protective colloid; otherwise, it would lose its effect in a few days, due to the destruction of such protection by bacterial action.

PROTECTION FROM AGGLOMERATION .

It will be noted in the discussion on emulsions that concentrated dispersions demand the presence of an emulsifying agent. In such cases the stability of the emulsion depends on factors relating to an adsorbed film at the oil-water boundary, as previously discussed. These protecting films offset the action of electrolytes to a great extent. If the concentration of the electrolyte is low, it may be present for a long period of time before breaking the emulsion. The electrolyte or agglomerating agent may be kept low by dilution, or by avoiding re-

[7] Alexander, *op. cit.*, p. 624.

agents which would cause chemical reaction resulting in an electrolyte being present. Liquids in dispersion (emulsions) as well as solid materials, will coalesce or agglomerate if brought in actual contact. It is the surface film of the protective agent which offsets this action. Since coalescence or agglomeration takes place spontaneously, work must be performed in the mechanical dispersion followed by protection of the dispersed particles by the stabilizer It is obvious that the work necessary to break up a liquid or solid mass into drops or grains is far less if some stabilizer is added. This reduces the surface tension of the liquid in which the material is dispersed.

VARIATION IN QUANTITY OF STABILIZER

As an illustration of the varying effects of emulsifying agents, it might be pointed out that there are very decided differences in various soaps when used for emulsification As a general rule, for best results the maximum quantity of soap for most oil-in-water types of emulsion varies from .25 to 1.0 per cent Beyond this point it is not only of no benefit but may be detrimental to the emulsion. The important point about soap emulsions is that a potash soap is, as a rule better than a sodium soap, for the films formed are more flexible A coconut-oil soap, as a rule, will form a better emulsion than some of the other types and will stand the addition of more electrolytes before breaking the emulsion It is advisable to use distilled water in making such emulsions There are frequently sufficient electrolytes present with hard waters to break the emulsion, whereas they would be more or less permanent if such electrolytes were not present.

This critical value of soap in the making of emulsions is a point which should not be overlooked As an illustration of this point, if one emulsifies a high percentage of oil into water, such as 70 per cent oil, the water phase should not contain, as a rule, less than 0 7 per cent nor have above 1.0 per cent of a potash soap In a 40 per cent oil emulsion, 0.5 per cent soap is frequently sufficient; if the concentration of this soap is increased much above 2 per cent it very frequently is detrimental to the emulsion. Of course, soaps vary greatly in emulsifying power and these rules are not supposed to be infallible. There are some brands of soap which are practically useless as emulsifying agents The above proportions apply to such soaps as potassium oleate, when of proper purity. The lowering of the surface tension is a factor, and as a general rule, with the increase in molecular weight of the fatty acid radical of the soap, the surface tension lowering effect is increased If the quantity of soap added as an emulsifying agent is decreased below the limits above stated, and the oil phase is increased, the result is that when the globules are split up there is more surface

area to cover. If this becomes sufficiently large, so that there is not sufficient emulsifying agent to form a complete film about each globule, it is obvious that the emulsion will not be very stable, and coalescence will follow.

It is quite obvious that the soap does not all go into the interface in an emulsion of the oil-in-water type. There is a relation between the concentration of soap in the interface and the amount peptized by water, and, therefore, a distribution of the soap between the water and the interface. From this, one will readily appreciate that anything which decreases the peptizing action of the water upon the soap will, of course, increase the amount of soap in the interface. On the other hand, if the peptizing action of the water is very large, this will decrease the amount of soap in the interface. Therefore, beyond the point of saturation of soap in the water phase, more soap will be thrown into the interface. This may cause a heavy film about the dispersed globule, which may be built up to a point where it becomes brittle instead of flexible. Once the protecting film is broken, the oil, of course, is liberated therefrom.

When oleic acid is placed upon the surface of water, a portion is adsorbed by the water phase and will have a tendency to spread in a film. The molecules will orient themselves so that if sufficient area is present, it will spread out to a thickness of one molecule on the surface of the water. If there is not sufficient surface it will draw up into drops. This was discussed quite fully under orientation. Thus, if there is a great excess of soap, the film may become heavy and viscous. Saponin forms a very viscous surface film,[8] so that in emulsification work it is only necessary, as a rule, to use a few tenths of a per cent; in some instances 0.05 per cent is sufficient to give a proper surface film. It is claimed that a 2 per cent saponin solution has a surface viscosity six hundred times that of the mass of the liquid; it drops to less than forty times below the surface.[9] Therefore, the quantity of saponin used, as a rule, should be in very small proportions. When a skin rapidly forms over the surface of an emulsion, it is a sign that the dispersion is becoming less stable, and the film is probably thinner, the greater the peptizing action of the liquid.[10]

VARIATION IN VALUE OF PROTECTION

Loeb[11] pointed out that gelatin has been found especially active as a protective colloid, while non-crystalline egg albumin has very

[8] Shorter, *Phil. Mag*, 11, 317 (1906).
[9] Staples and Wilson, *Phil. Mag*, 15, 406 (1883).
[10] Bancroft, "Applied Colloid Chemistry," 2nd ed, McGraw-Hill Book Co, New York, 1926, p 229.
[11] Loeb, "Proteins and the Theory of Colloidal Behavior," 2nd ed, McGraw-Hill Book Co., 1924, p 349

little protective action. He demonstrated this by protecting small particles of collodion, and showed that collodion particles not treated with a protective agent are very sensitive to the action of electrolytes. This is probably due to the fact that the particles are held in suspension only by virtue of their electrical double layer, or Helmholtz effect. When such collodion particles are dispersed in a gelatin sol, they apparently display a high degree of adsorption and form a gelatin film which is not destroyed very easily, even by high concentrations of salts. Therefore, such particles coated with a gelatin film are very stable and are not dependent upon the electrical effect for their stability. With egg albumin present in the water, it was found that such colloidal particles, when they coat on collodion, lose their high affinity for water. In other words, the egg albumin has no longer a great affinity for the water, and, therefore, exhibits a denatured effect, such as would be obtained after it has been heated or cooked. Thus, collodion particles coated with egg albumin are dependent solely on the Helmholtz effect for holding them in dispersion and are subject to precipitation with very low concentrations of electrolytes. It is possible that when the egg albumin is adsorbed on the surface of the dispersed particles of the collodion, the group present in the albumin which has the affinity for water has in some way been affected in the orientation while forming the film. As a result it is stated that the albumin has been denatured. The same effect, of course, is brought about with albumin and other protein matter when it is subjected to high heats, or taken beyond the critical temperature at which denaturing occurs. This is a point of great importance in the making of emulsions when using albumin or other proteins for the emulsifying agents at high temperatures.

In dispersions it is frequently stated that the precipitating effect on the dispersed particle, whether it be solid or liquid, varies with the method in which it comes in contact with the electrolyte. The precipitating effect is obtained by adding the electrolyte all at one time, thereby bringing a great concentration of the precipitating ion and rapid adsorption, so that the dispersed particles are soon brought to the isoelectric point. If the same amount of electrolyte is added slowly, there results a gradual increase in the size of the particles, due to partial neutralization by the adsorption of the ions of opposite charge.[12] Thus this is a slower process of coagulation. In any event, after sufficient electrolyte has been added, agglomeration takes place, but the particles may remain for a longer period of time in dispersion if the electrolyte is present in a more dilute concentration. The above statement is true with dispersions of particles not properly protected. Therefore, the action of the electrolyte upon a dispersed product de-

[12] Weiser. *J. Phys. Chem.* 25, 404 (1921)

pends, to a great extent, upon the protective colloid or other film formed about the dispersed globule. The more resistant this is to attack, the more stable the dispersion. A change in the adsorbing power of a colloidal substance will also greatly vary its stability. If ferric oxide of two degrees of dispersity is present (that is, with two different adsorbing powers), we have different degrees of stability. Bancroft[18] claims that "two colloidal ferric oxides have been distinguished." Of considerable importance, however, is the adsorption of the stabilizing ion of the electrolyte; if this is sufficient to give considerable potential difference, the product should be fairly stable. The effect of the electrolytes is also largely dependent upon their valency, and a univalent ion requires much larger concentration to bring about flocculation than the bi- and tri-valent. The effect of coagulation is usually increased as the valence of the ion increases. There is also the question of when two colloids of mutual adsorption are present; for instance, if each were peptized by water to an equal extent, the mutual adsorption may be sufficient to cause precipitation.

LIQUID IN WHICH STABILIZER IS DISPERSED

The substance in which the emulsifying agent is peptized is of vital importance in emulsification, and determines which type of emulsion will be obtained. As a general rule, where the emulsifying agent is more easily wetted by water than oil the water would be the external phase, while the reverse is true, if the emulsifying agent is more easily wetted by oil. The general rule on this, which was previously cited under Emulsification, is as follows: If the surface tension of liquid A and the emulsifying agent is lower than the surface tension between liquid B and the emulsifying agent, then liquid A will be the dispersing and liquid B the dispersed phase. The emulsifying agents used for protection in dispersions are, as a rule, colloidal substances. That which is peptized by the water phase will emulsify oil in water, while that which is peptized by the oil phase will emulsify water in oil. This might be further illustrated by again pointing to the monovalent soaps which are peptized by the water phase, and as a general rule will make an oil-in-water type of emulsion. A calcium soap which is insoluble in the water phase but can be peptized by oil will promote a water-in-oil type of emulsion.

TYPES OF PROTECTIVE COLLOID

The emulsifying agents usually emphasized for oil-in-water types of emulsion are sodium and potassium soaps, egg albumin, gelatin, glue and most water-soluble proteins, gum arabic, Irish moss, casein, starch,

[18] Bancroft, *op. cit.,* p. 297.

saponin and various bark extracts, such as licorice root. Any sub-
stance which causes foaming of the water, and therefore indicates lower-
ing of the surface tension, is worth looking into in making emulsions
of the oil-in-water type. It is frequently stated that alkali, such as
sodium hydroxide, is an excellent emulsifying agent for fatty oils. This
has long been disproven as a result of Donnan's investigation,[14] which
showed that the emulsifying powers were due to the soap formed by
the interreaction with the small amounts of free fatty acids. These
are always present in fatty oils after a very short period of standing.
Also, in some instances, there are other groups present in which the
alkali will combine to bring about results similar to those obtained with
a soap   Hence, the only value of the alkali in emulsification is where
some substance is present with which it can combine, as above stated

When casein is used as an emulsifying agent, it is necessary to
have alkali present to assist in the peptizing action, possibly forming
sodium caseinate. It was·claimed by Loeb[15] that "the forces which
drive the sodium caseinate into solution are not those of the Donnan
equilibrium, for if this were true, the rate of solution of the casein
granules would reach a maximum at a hydrogen-ion concentration be-
tween 10 and 12 and would then diminish; whereas, as a matter of
fact, the rapidity of peptization increases rapidly with the addition of
alkali. This is true to such an extent that even a half-normal sodium
hydroxide solution will almost peptize casein instantly." This also
agrees with the fact that a solution of sodium caseinate in water
requires an exceptionally high concentration of electrolytes to cause
precipitation. If isoelectric casein is placed in a hydrochloric acid
solution "the force of cohesion between the molecules of casein is
sufficient so that peptization, or so-called solution of the casein, is im-
possible until the molecules are forced apart mechanically" This is
due to the hydrostatic pressure of the water driven into the particles
on account of the Donnan equilibrium. "The swelling of the casein
particles is necessary for the solution of casein acid salts and the par-
ticles are dissolved only when their swelling exceeds a definite limit."

IMPORTANCE OF PROTECTIVE AGENT IN MECHANICAL DISPERSION

In mechanical dispersion it is most essential that the proper pro-
tective colloid be present, and if these substances are readily peptized
by the solution in which they are dispersed, they are of great assistance
in making such mechanical dispersion. Very frequently, for instance,
in the presence of gum arabic, it is possible to make dispersions in
water by the use of the colloid mill, whereas with water alone it is

[14] Donnan, *Z phys Chem*, 31, 42 (1899)
[15] Loeb, *op. cit*, p 351.

impossible. This does not only apply in the case of mechanical dispersions but in so-called colloidal solutions of silver chloride, bromide, etc. These are obtained by precipitation in the presence of a protective colloid such as gelatin. Chromate salts, copper oxide and ferric oxide when in a hydrous state may be obtained in a fine degree of dispersion by the use of sugar in the water phase. Cadmium sulfide may be dispersed in the presence of casein, and a great number of substances may be held in suspension by use of the sodium salt of albumin, which frequently can be used to replace gelatin. Colloidal gold, silver, etc., may be kept from coagulating by means of starch, and Acheson's Aquadag is kept in colloidal dispersion by the use of tannin and oxide of iron.[16] In fact, there are so many types of protective colloids that can be used, according to the charge taken by the dispersed substance, that it is a study in itself and one which should be quite familiar to anyone applying the principles of mechanical dispersion. After all, the type of stabilizer used has a great deal to do with the success or failure of the dispersion, not only in the protection after such dispersion is accomplished, but also in assisting in making such mechanical dispersion. A large number of vat dyes which cannot be dispersed in water directly can, by the use of the so-called colloid mill, be dispersed with a great degree of success by the addition of proper stabilizers, thus indicating that the machines have dispersed the product in the first instance but that there has been instant re-flocculation. By dispersion in the presence of such stabilizers, this can be eliminated or offset in a large number of instances. Hence, in work on mechanical dispersion, it is most important to concentrate on the stabilizer or protective colloids and their effect in such dispersions. Such efforts may be more productive than efforts to make finer adjustments than are possible on the machine.

STABILIZING BY USE OF FINELY DIVIDED SOLID MATERIAL

In the previous discussions on dispersions, very little has been mentioned regarding the utilizing of finely divided solids for protecting the dispersed globules or solids. It has been demonstrated, from time to time, that emulsions can be made by the use of very finely divided material in the interface, the material being adsorbed on the oil globule · as the protecting agent. Such materials as finely divided carbon black, fine clays, Bentonite, etc., can be used for such work in emulsification. It has been reported that the Arabs in Northern Africa use argillaceous earth in place of soap for washing purposes and that such material will readily emulsify oil in water. There are a great number of fine earths which can be used for similar purposes. Some of them, how-

[16] Doyle, *J. Phys. Chem.*, 17, 390 (1913).

ever, have a tendency to reverse the emulsion in cases where they are more easily wetted by the oils than by the water. This is specially true of carbon blacks, lamp black, etc. It is claimed that in some instances in emulsification by the use of gums, they are not all peptized by the water, but that a small proportion of the fine powder is in the interface in combination with the peptized gum. However, with carbon black, fine clays, etc., all the evidence goes to indicate that it is a fine coating of the solid particles at the interface which protects the dispersoids.

Emulsions made by the use of fine clays or solid particles, however, are as a rule not very stable. Thus, it is far better for one considering the making of an oil-in-water type of emulsion to use one of the more common emulsifying agents which are peptized by the water.

It has not been attempted to list all emulsifying agents in this discussion of protective action of colloids, since new ones are being discovered almost daily. References have been made to more of the typical ones and those commonly used. A series of trials with the different emulsifying agents should be made in the laboratory to determine the proper type to use in any special case. This will be much more satisfactory than making any arbitrary choice.

While the protective colloid is of great assistance in making permanent emulsions, by offsetting the action of electrolytes and the protecting of the dispersed particles from coalescence, such protection should not be taken advantage of. In other words, the emulsion should be made under as ideal conditions as possible so as not to have to depend solely on the protection of the colloid to avoid breaking of the emulsion One of the most important guides, after determining the type of emulsion, is regulating the hydrogen-ion concentration in order to assist properly in stability. The general rule for all oil-in-water types of emulsion is to keep the emulsion slightly on the alkaline side; for, in the majority of cases if not in all instances such emulsions carry negative charges. Hence, a pH value of slightly above 8 seems to give the better condition for stability in most instances. If the alkalinity is increased to excessive amounts, there is danger of the alkali affecting the film at the interface. If this is once affected, the stability of the emulsion is in danger.

In the case of dispersion of solids into liquids there is also a somewhat similar condition. In such instances, as a rule, one must protect the small solid particles in order to avoid agglomeration. This solution must be handled as a parallel case, taking into consideration the fact that, in a large number of such instances, the dispersed particles have a positive charge; that is, that the potential difference between the particle dispersed and the liquid is positive. The same points apply, however, and in such instances where the product has a positive charge.

one should strive to keep the pH value at about 6. If one goes much below a pH value of 5, there is again danger of some action on the film at the interface.

Of course, no general rule can be given for practical applications of dispersion that cover all cases, as the science is really still in an empirical state. However, rapid strides have been made in the past few years since the problems in dispersion have been approached from the physical-chemical viewpoint. The principles discussed throughout this work have proven themselves of value.

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Chapter XI.

The Dispersion of Solids and Liquids in Gas.

Probably the most elementary form of dispersion, or the one considered the simplest, although, as a matter of fact, it obeys all the laws of other types, is that wherein the dispersion medium is a gas. The dispersed phase may be a solid, such as carbon in flue gases, or a liquid, as in an atmospheric mist or cloud. These dispersions are usually spoken of as aerosols Fine dispersions, such as clouds in the atmosphere, are spoken of as cloudy aerosols, whereas dispersions of large particles, too large to show any Brownian movement and characterized by such types as smoke, are sometimes called smoky aerosols. Sometimes these aerosols become flocculated and form a network similar to that of a gel These sometimes occur in the accumulation of soot found in a stack or flue. Using the same terms as in other dispersions, these might be classified as aerogels [1]

AEROSOLS

Aerosols, like all dispersed systems, may be formed by mechanical dispersion of a solid or liquid, which as a rule, is in a relatively coarse condition. The material may be split up mechanically into a fine division and dried in such condition by the spray-drying process Another way in which these aerosols might be formed is by condensation of finely dispersed particles, such as a vapor. A typical example of aerosols is the air about a dusty road, the fine dust ejected from volcanoes, the dashing of waves against a cliff causing a spray, the bursting of high-explosive shells and the air in the vicinity of dry-grinding mills where material is being pulverized A flame might be considered an aerosol when it is luminous and is emitting fine particles of carbon that are dispersed in the gases. This causes considerable heat radiation, whereas in the case of a non-luminous flame there is very little radiation.

Aerosols can be classified according to their particle size. Those which are larger than 10^{-8} cm in diameter will settle in still air with increasing velocity and will not diffuse.[2] Particles larger than 10^{-8} to

[1] W E Gibbs, in Alexander's "Colloid Chemistry," Vol 1, Chemical Catalog Co , New York, 1926, p 393.
[2] Gibbs, *op. cit.,* p. 412

10^{-5} cm will settle in still air at a constant velocity and, if they are perfect spheres, will obey Stoke's law of sedimentation These particles will not diffuse. Particles in the range from 10^{-5} to 10^{-7} cm. in diameter show active Brownian movement and diffuse fairly rapidly, similarly to gases, and will not settle at all in still air.

When a liquid is atomized or sprayed into a drying chamber, the condensation from the vapor is determined by the degree of super-saturation produced in the air or gas. The number of droplets formed from the vapor, as well as their average size, will depend largely upon the suitable nuclei that are present in the vapor, for these vapor particles must have something to condense on. Hence, the droplets will be smaller when a limited amount of vapor condenses upon a large number of nuclei.

To make the matter a little clearer, we might take some typical examples of conditions observed in nature. For instance, fog consists of drops of liquid suspended in air. To obtain this fog a vapor must be saturated suddenly so that the condensation takes place uniformly throughout the mass. If the supersaturation is very excessive, the liquid, of course, comes down as a dense fog, while if it is slight, very little fog forms. Apparently in all cases there must be small dust particles or nuclei on which these droplets may condense. In ordinary air, the dust particles are numerous, hence condensation takes place readily. If the air is entirely free from dust through filtration, or washing, condensation will not·take place until the volume has been increased about one-quarter; that is, until the degree of supersatura-tion becomes approximately 4.2 times as great [3] If the air is ionized, the particles may condense upon the ions, which form the nuclei in this case, and since these gaseous ions act as nuclei, condensation may take place when inert air is exposed to ultraviolet light, or when a silent discharge is passed through the air, or any other such ionic disturbance, such as the action of cathode rays or x-rays. The nuclei upon which the condensation occurs are usually gaseous; for instance, for expansions of the gas from 1 25 to 1.28 water vapor condenses only upon negative ions. In the case of expansions from 1.28 to 1 34, the water vapor condenses upon positive ions, and in air which is dust-free, if the ionization be increased by the action of x-ray or from radioactive substances, the degree of dispersion will be greatly increased so that cloudy condensation takes place instead of fine rain [4] Millikan [5] utilized some of these principles in measuring the size of the electron These have also been employed in indicating the visible paths of α and β particles travelling through super-saturated air The particle ionizes

[3] W. E. Gibbs, *op cit* , p. 396
[4] W. E Gibbs, *ibid.*
[5] Millikan, "The Electron," University of Chicago Press, Chicago, 1924, p. 121

air as it passes through, leaving behind the cloudy condensation, thus making visible the path of these particles as they travel through the air.

STABILIZING THE AEROSOL

In general, it may be said that the nucleus promotes condensation of vapor upon itself by introducing locally into an otherwise uniform vapor a sudden pressure gradient, owing to the diminished pressure of the portion of vapor that is directly in contact with the nucleus.

When condensation of water vapor is carried out at temperatures below zero, ice crystals are produced in the form of a cloud. On the other hand, a cloud of liquid particles forms through condensation of water vapor at temperatures above zero. The particles can be cooled very carefully to a temperature as low as 30°C. without solidifying. The particles are super-cooled in this instance, and of course, are in a state of unstable equilibrium, similar to the conditions in a super-saturated solution, but when these super-cooled particles come into contact with a solid surface, they immediately solidify and the surface becomes coated with ice.[6]

In all cases the stability of aerosols depends primarily upon the degree of dispersion and the conditions under which it is dispersed. The particles of highly dispersed systems have a tendency, on account of their active Brownian movement and the large number of particles present, to flocculate until their size increases sufficiently so that the Brownian movement is no longer active. These aggregates then settle slowly under the influence of gravity. In order not to have the aerosols flocculate, the particles must be surrounded by films of adsorbed gas and also contain like electrical charges so that they will repel each other. If the dispersion is made in a gas medium which is strongly adsorbed by the particles, it will be possible to prepare aerosols of maximum stability. The higher the boiling point of the gas, as a rule, the more readily it is adsorbed; also the amount of adsorption is greater when the gas is submitted to higher pressures, and with the temperature reduced.[7]

CHANGING THE STATE OF THE AEROSOL

Particles which are surrounded by a layer of adsorbed gas will still be able to attract one another, but will be unable to coalesce unless the coalescing force is great enough to drive through this protecting film. Where the force is great enough to do this, the aggregates are a fluffy product in which the individual particles are really separated from

[6] Simpson, *Nature Mag.*, April 4, 1923; also *Phil. Trans.*, 209A, 379 (1909)
[7] W. E. Gibbs, *op. cit.*, p. 409.

one another by layers of a gas. We have such instances in the case of zinc oxide. Tolman [8] has shown that stability of an aerosol is destroyed by stirring or agitation where the particles are brought in contact with the walls of the containing vessel, to which they adhere. Also, for a given degree of dispersion, the stability is diminished when the concentration is increased. The particles then have more opportunity for collision and also for contact with the walls of the container. These are problems of interest to anyone undertaking spray-drying operations. Dusty air is more sensitive to thermal agitation than dust-free air, as previously explained. The prevention of frost by the use of smudge pots depends upon the ability of the smoke to absorb light and reflect heat, hence offsetting the attack of the frost.

Charged particles in suspension in gas can be moved in any given direction by the application of electrostatic force. The particle can be made to move vertically under the force of gravity, made to just equalize it or be allowed to drop by the action of gravity by controlling the particle with the electrical charge by the application of proper electrostatic force. Since this movement in the electrostatic field is proportional to the mass of the particle, it is possible to determine the amount of charge carried by the particle, the mass of the given particle, or the magnitude of its Brownian movement.[9] These principles are of fundamental importance in measuring particle size in aerosols.

THE ELECTRICAL CHARGE OF AEROSOLS

As to the electrical charges, the conditions are somewhat similar to the case of dispersions in liquids. For instance, if freshly prepared smoke is placed between charged plates on a microscopic slide, some of the particles will be observed to be positively charged and others negatively charged, while others seem to be neutral. This case is somewhat different from ordinary dispersions in liquids, for we may get conditions of different charges and those which have neutralized each other or exist at the isoelectric point. When the charges are all alike, however, they repel each other and flocculation does not follow readily This is the condition for stable aerosols. Flocculation can be induced in such charged particles by treating them with particles charged with an opposite sign, such as the method described in Chapter VI for dispersion of fog (see page 72). Hence, aerosols differ somewhat from liquid dispersions, in that they have simultaneously charged particles of opposite sign; they also differ in the matter of the adsorption of the dispersed phase.

[8] Tolman, *J Am Chem Soc*, 41, 304-312 (1919).
[9] Millikan, *op. cit*, p. 111.

Chapter XII.

The Theory of Emulsions and Emulsification.

Emulsions have been the subject of lively comment in chemical literature in recent years, and while no general theory of emulsification has been elucidated, many have been proposed from time to time which subsequently were shown to apply only in special cases. There is, however, a mass of arbitrary data which can be profitably applied in the commercial preparation of emulsions by mechanical means. This practice has been carried on by the author for a number of years with the use of homogenizers and so-called colloid mills

In the preparation of emulsions, it is necessary to have some conception of the modern theories of emulsion and emulsification so as to be able to overcome the difficulties as they arise. It will be found that there are a great many points to keep in mind, for emulsions at best are very liable to cause trouble from time to time, unless prepared on a strictly scientific basis and with the physico-chemical viewpoint constantly in mind A great many difficulties and troubles in emulsification work may be fairly easily overcome through the application of such principles

An emulsion is a heterogeneous system containing two liquid phases, one of which is dispersed as fine globules in the other That liquid which is broken up into globules is termed the dispersed phase, while the liquid surrounding the globules is known as the continuous phase or dispersing medium While the emulsion consists of drops of one liquid suspended in another, a stable emulsion is really a three-phase system, for there must be present, in addition to the two immiscible liquids, an emulsifying agent or stabilizer In very dilute emulsions, or where the oil phase is not of high percentage, these drops or globules may be stabilized by an electrical charge; these behave like any colloidal solution of the same type.[1] In the usual emulsion, however, or one containing any quantity of oil, an actual film is formed around each globule which prevents them from coalescing. The two liquids must be immiscible, or almost so, and when emulsified are referred to as the internal and external phases respectively. If the oil globules are dispersed in the water, it is called an oil-in-water type of emulsion, the

[1] Bancroft, "Applied Colloid Chemistry," 2nd ed, McGraw-Hill Book Co, New York, 1926, p. 351

water being the continuous phase. The reverse type, that is, where the oil is the continuous phase, and the water dispersed therein, is classified as a water-in-oil emulsion The factor which controls the type is the nature of the emulsifying agent. The oil-in-water type is the more common.

EMULSIFYING AGENTS

The emulsifying agent is a substance which goes into the interface, thus producing a film around each of the dispersed globules In all emulsions where the concentration is over 2 per cent, an emulsifying agent is necessary[2] Sometimes these occur in the product naturally and do not have to be added. For instance, in dairy emulsions such as butterfat dispersed in milk, albumin and casein, which are both excellent emulsifying agents, are present In chocolate emulsions, where cocoa fat is emulsified in the chocolate liquor, fine particles of cocoa powder accumulate about the dispersed globules of cocoa fat and act as the protecting film or emulsifying agent.

Good foam producers, such as saponin, sodium oleate, gelatin, and sulfonated oils, are found to give very strong plastic films, hence are classified as good emulsifying agents. It is because of the lowering of the surface tension that these products produce good foams. Thus, in selecting emulsifying agents, we, as a general rule, look favorably towards good foam producers as a fertile field for investigation in selecting of emulsifying agents It is possible, however, to form irregular and even shapely pointed drops of one fluid medium in another when a high percentage of emulsifying agent is present; the emulsifying agent in the interface in such cases must be of a solid nature.[3] In the usual type of emulsion, however, the microscopic examination shows that the dispersed particles are in the form of spheres, such as we observe in butterfat dispersed in milk and in the usual oil-in-water type. We see exceptions to this rule, however, from time to time, such as in the case of rubber latex. When the rubber trees are tapped the milk obtained (which is known as latex) contains approximately one-third rubber particles and it is found that these globules are always pear-shaped This is a strong argument in favor of the orientation theory, as previously discussed

Bivalent and trivalent soaps such as calcium, magnesium or aluminum oleates which are peptized by the oil phase can be used for emulsifying water in oil Rosin and the so-called rosin soaps act in a similar way This fact is taken advantage of occasionally in the

[2] Clayton, "Theory of Emulsions and Emulsification," Blakiston, Philadelphia, 1923, p 14, 15.
[3] Wilson, in Alexander's "Colloid Chemistry," Vol. 1, Chemical Catalog Co, New York, 1926, p 277

mixing of paints where it is desired to incorporate water to cheapen the material. It is claimed that with some paints as much as 50 per cent of water can be readily mixed without changing the appearance, for the reason that the oil is the external phase. Calcium and aluminum soaps are used in lubricating greases Such greases may consist of lime soaps containing 15 to 25 per cent water emulsified therein Also some of the lubricating greases for automobile use consist of aluminum soaps dissolved in mineral oils with water emulsified therein, to which occasionally some rosin has been added to assist in this type of emulsification. If the water is stirred into a heavy lubricating oil containing such lime soap, it will emulsify as a water-in-oil type. Lanolin or wool fat will emulsify water, taking up large quantities, even to the extent of 80 per cent dispersed in the lanolin. While it has not been definitely proven what the emulsifying agent is in this case, the results seem to indicate that it is cholesterol, contained in the wool wax, which acts as the emulsifying agent. The case of lanolin is one of the exceptions of stable emulsion of the water-in-oil type, for, as a general rule, such emulsions are not stable for long periods of time. They are frequently spoken of as the reverse type of emulsion, for in emulsification one usually thinks of the oil-in-water type.

EARLY METHODS OF EMULSIFICATION

In the early work on emulsions and emulsifications we come in contact a great deal with the emulsions used in pharmacy, for the pharmacists made great use of the emulsions of the oil-in-water type, and the various older books on pharmacy have elaborate details on the making of emulsions. While these methods are all obsolete and do not conform to modern practice they should be mentioned, for they undoubtedly contribute to the development of the art

The pharmacists had two general methods for making emulsions One was known as the "American method" in which they used a gum, such as tragacanth and acacia, the gum, of course, being present as an emulsifying agent. The procedure by this method was to peptize the gum in the water phase, this colloidal solution was placed in the mortar and the oil added in small quantities with the idea of building up the emulsion This was, of course, a very slow method and was usually done by hand. It does not make what we would today classify as a true emulsion The resulting product under the microscope has oil globules of all sizes, from a few that are very finely split up to larger ones of all possible dimensions, held in mechanical suspension. Acacia was the popular emulsifying agent for the pharmacist. Very frequently he added some gum tragacanth to thicken the product, which was very fortunate, for emulsions having globules of such large

dimensions most assuredly need something to thicken them so that there will be greater resistance to the coalescence of the oil globules. In other words, these emulsions cannot be made in a thin fluid condition that will readily pour.

In the early discussions on emulsification are found such absurd statements as "a left-handed man cannot make an emulsion." In other words, they must always be stirred to the right. This theory, of course, has been upset for some time. In modern practice in the commercial production of emulsions, if one had to contend with such conditions, the operation would be made prohibitive.

The other method used by the pharmacist was known as the "Continental method." In this the gum was ground in a mortar with the oil, and water was thereupon added so as to make the entire emulsion at once. This method had a certain amount of merit to it. The Continental method was studied by Briggs,[4] who found that the grinding of the gum in oil increased the interface between oil and water by suspending in the oil finely divided solids which are preferably wetted by the water. In other words, the gum acts as a finely divided solid and also as an emulsifying agent. As stated by Bancroft,[5] it is possible to get the same results by grinding the oil with sand and adding a colloidal solution of gum, but the resulting emulsion would then contain the sand.

Emulsifying value in such a combination is largely in the gum acacia, while the gum tragacanth merely thickens the product so as to offset the coalescing of the oil droplets, which are not split fine enough by this method to overcome the usual action of gravity. The resulting product, of course, is a very viscous emulsion which the pharmacist usually has to resort to packing in a wide-mouthed bottle, so that it will flow.

HOMOGENIZING

In making emulsions on a commercial scale it is necessary to operate by a more practical method than the mixing by hand, such as the mortar and pestle method of the pharmacist. We therefore find emulsions being made in tanks with all kinds of agitating devices, such as paddles, propellers running at various speeds, various types of shaking devices, the use of the dairy churn and other such principles. The first equipment that would produce a uniform emulsion, however, was a machine known as a homogenizer. It is based on the principle of splitting up the oil droplets by the use of pressure from 1800 to 3000 pounds per square inch, forcing the product by either a rotating

[4] Briggs, *J. Phys. Chem.*, **24**, 147 (1920).
[5] Bancroft, *op. cit.*, p. 359.

head or a fixed valve in a film thin enough and with pressure sufficient to break up the oil globules.

This machine originally derived its name from the fact that it apparently made the product homogeneous or uniform throughout· Of course, as a matter of fact, no emulsion could really be called homogeneous. Nevertheless, the machine split the oil globules up into a very finely divided state It should not be confused with the present type of colloid mill, which is sometimes called a homogenizer and is based upon somewhat different principles, for the homogenizer is adapted only for making emulsions and will handle only liquids. Solid particles cannot be dispersed through a homogenizer. It is a very excellent machine, however, for making various types of emulsions, that is, so far as splitting up of the oil droplets is concerned.

The first users of pressure homogenizers were in the dairy industry [a] This use dates back to about 1905, when the homogenization of such dairy products as evaporated milk and light creams were accomplished by such means. Its purpose was just the reverse to that of a cream separator. Instead of separating the fat from the milk, it was possible with the homogenizer to incorporate fat into milk, thereby making any percentage of cream desired up to as high as 40 per cent, or what is known as heavy cream It is a well-known fact in the dairy trade that homogenized cream cannot be whipped when prepared under regular conditions, such as at the pressures above cited, nor will the fat separate out when passed through a cream separator. In other words, by this means one obtains almost a perfect emulsion of milk or cream.

After the homogenizer had been successfully used in this field for a few years, it was next introduced into the ice cream industry where it was used to incorporate the fat, milk solids, etc , into a homogeneous mass and develop a smooth ice cream, thus bringing about a big improvement in the product. The practice of homogenizing was confined to the two above-mentioned industries for a number of years It was then adapted by the pharmacist to the making of various types of emulsions, such as cod-liver oil, mineral oil-agar emulsions, etc These machines made fairly satisfactory emulsions of the oil-in-water type for pharmaceutical manufacture and in the preparation of hand lotions and various face creams.

So that one may gain a fair idea of the efficiency of such machines for the preparation of emulsions, it might be advisable to discuss the change in the size of fat globules when proper emulsifying agents are present. In dairy emulsions there is, of course, sufficient casein and albumin present in the milk to take care of the emulsification, hence it is not necessary in such instances to add an emulsifying agent

[a] Travis *J. Chem. Education,* **3,** 336 (1926).

Wiegner,[7] in his studies of homogenized milk, investigated the change in the diameter of the fat globules and their increase in number following homogenization, in order to compare the globule size of some of these typical three-phase emulsions

UNIFORMITY OF HOMOGENIZED PRODUCTS

He reported that the diameters of the fat globules through homogenizing have been reduced from 2 86 microns to 0.27 microns, and in another instance from 2 94 microns to 0.17 microns, the sample with the smaller fat content being split into a finer state of division. In the test cited above the number of particles in the first sample was increased 1,188 times, and in the second sample 1,258 times after homogenization. The surface area of the fat globules was increased 112 and 117 times respectively. There was no apparent change in the density and no difference in electrical conductivity, although Buglia[8] in similar work noted a slight increase in the electrical conductivity of homogenized milk. Both Wiegner and Buglia found that there is a slight decrease in osmotic pressure following homogenization.

Baldwin[9] found that the butterfat globules in cow's milk were from 0.005 to 0.006 mm. in diameter (5 to 6 microns). By homogenizing, that is, further sub-dividing, the diameters were reduced to 1 to 2 microns.

This gives one an idea of the effective splitting up of fat globules in milk by the use of a pressure type of homogenizer. While the same effect can now be accomplished by use of the modern so-called colloid mill, as far as the author's experience goes in checking the various types of equipment, the splitting up of the fat globules does not seem to be any more efficient than that accomplished by the use of the pressure type of homogenizer. The modern colloid mills, however, have some decided mechanical advantages and seem to be more adapted for continuous heavy duty.

OPERATION OF HOMOGENIZERS

It has been the experience of most people in the past that a pressure type of homogenizer is very satisfactory when under proper supervision, but it must be treated with more or less care, for, at such pressures, if the least little thing happens to the pressure valve, the efficiency of the emulsion, of course, immediately is greatly reduced. Because the principle of these machines is to maintain high pressure, if for any reason channel grooves or particles of dirt accumulate under

[7] Wiegner, *Kolloid-Z.*, **15**, 105 (1914).
[8] Buglia, *Kolloid-Z.*, **12**, 353 (1908)
[9] Baldwin, *Am. J. Pub. Health*, **6**, 862 (1916)

the pressure valve, then there is a possibility of some of the emulsion going through without being properly broken up. This difficulty seems to be eliminated in colloid mills by the fact that such particles would be dispersed. The author, however, has made a great number of successful commercial installations of pressure homogenizers, and under proper supervision there have been relatively few complaints. While the tendency seems to be towards the use of the so-called colloid mill for emulsification as well as for colloidal dispersion, the pressure type of homogenizer serves its purpose well in certain industries

The usual equipment for making an emulsion by the use of a pressure type of homogenizer includes a mixing tank in which the ingredients are first thoroughly mixed and heated to proper temperature for homogenizing The idea of this preliminary mixing is to get all the ingredients together in proper proportion. The mixing tank is very often glass-lined and equipped with various agitating devices, such as propeller or coil agitators. In the ordinary preparation of an oil-in-water type of emulsion, where the emulsifying agent is peptized in the water phase, the water after being put into the mixing tank is agitated and the emulsifying agent added. The oil is then slowly run in under agitation with proper temperature, according to the demand. The mixture is thoroughly agitated until ready for passage through the homogenizer. This is the procedure where an emulsifying agent such as soap or sulfonated oils, caseins and other such emulsifiers is used.

In pharmaceutical preparations, however, if gums are going to be used, such as a blend of tragacanth and acacia, these are usually added to the oil phase in the form of a powder. In such an instance the oil is put into the agitating tank first and the gums agitated therein The reason for the variation in this case is that the gums are insoluble in the oil and by agitating them therein equal distribution in the oil phase is obtained so that when the water is added, instant swelling action of the gums is produced. This gives a quick action and does away with the long delay when the gum is added to the water phase Of course, it passes into the water phase as soon as the water is added and forms a proper protective film in the interface between the water and gum, such as described in the continental method of making emulsions The procedure in this case is reversed, as above described, so as not to cause the trouble by the grouping together of the powdered portions of gum which form a seal or a sort of balling action, and make it difficult to get the gum in dispersion in the water It means that the water phase can come in contact with the individual granules of gum rather than the collection or group of them, and almost instant action is obtained. This is an exception, however, to the general rule, for in most instances in oil-in-water type emulsions the emulsifying agent is added to the water phase. The oil is run in under agitation
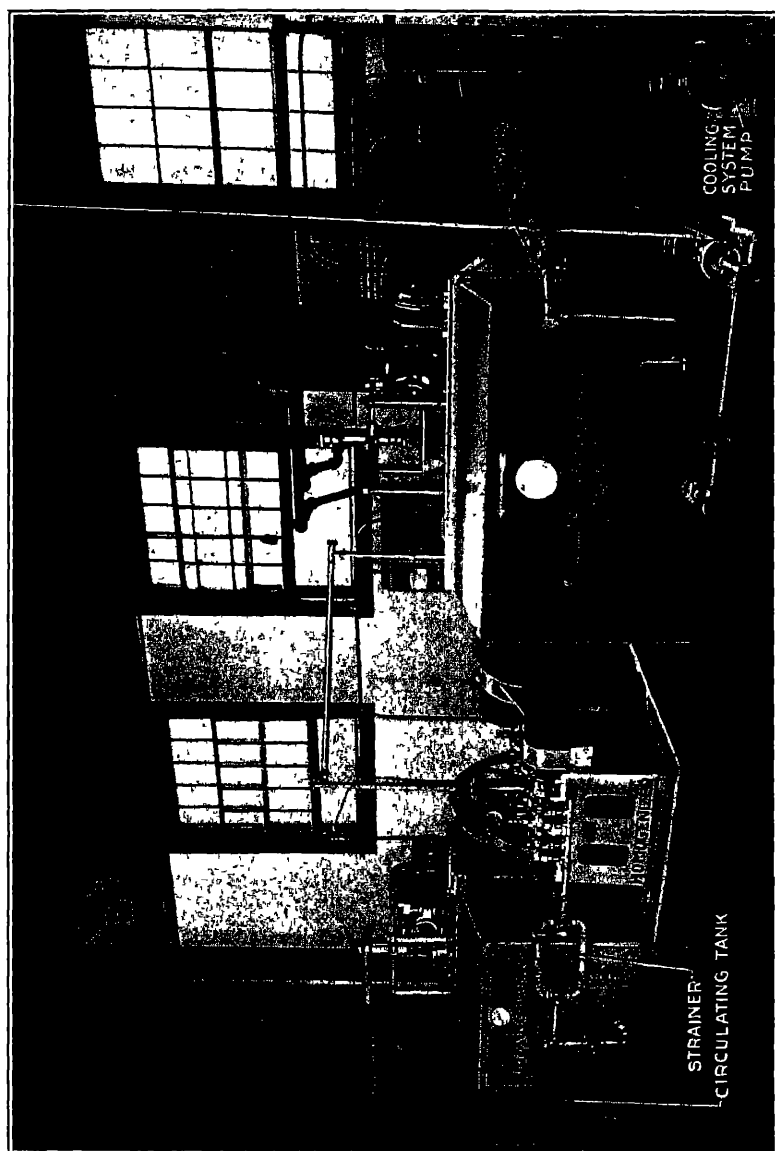
FIG. 5.—Complete Homogenizer Unit.

thereafter until the proportions proper for the emulsion desired have been added.

After the ingredients have been thoroughly blended in the mixing or agitating tank, they are fed in uniform proportions through sanitary pipes to the homogenizer. The pump used is capable of pulling this mixture through and putting it under pressure in the machine. The pressure may be anywhere from 1200 up to 3500 pounds per square inch Following the homogenizing it is forced under its own pressure into the storage tank The product may be cooled through use of a jacketed storage tank, or else with coil agitation. From the storage tank it is pumped to any point, such as a bottling or filling machine. The illustration (Fig 5) shows quite clearly the usual set-up. A great number of such units have been installed throughout the United States, as well as abroad, and have been in operation for several years

THE HOMOGENIZER AND THE COLLOID MILL COMPARED

Within the past few years the pressure type of homogenizer has been, in a great number of instances, replaced by the so-called colloid mill, which will be discussed more in detail in another chapter. This is largely brought about through the fact that colloid mills have certain mechanical advantages over the pressure type of homogenizer There has been some confusion, however, among manufacturers as to the difference between a homogenizer and a colloid mill. Hence, so as to eliminate, as far as possible, such misunderstanding, we will refer to the machine described above as the pressure type of homogenizer, meaning pressures such as described for making the emulsion. With the so-called colloid mill the emulsification is brought about by hydraulic shearing action which is of somewhat different principle, and while it is true that there is a slight amount of pressure involved, there is nothing like that used in a pressure homogenizer. Some of the modern colloid mills are also called homogenizers, this has caused the confusion. The pressure type of homogenizer will make a very fine emulsion when properly operated, but it will not handle anything of a solid nature nor will it handle a heavy viscous emulsion, due to the pumping action of the valves A pressure homogenizer is really nothing but a high-pressure pump, and the forcing of the mixture by fine orifices adjusted by building up of the pressure through the closing of the clearances

Regardless of which type of machine is used—a pressure homogenizer or a colloid mill—in both instances the emulsion is made by mechanical means. The ultimate product is very similar, and as pointed out frequently throughout this book, the matter of which type of machine is used is of secondary consideration. It is of primary importance that the proper emulsifying agents be used and that the condi-

tions be right for making the emulsion by such mechanical means. The selection of the type of unit to use is largely a matter of opinion of the purchaser as to the various mechanical features. It is somewhat a parallel case with the automobile industry. There are a great number of machines on the market, some with certain mechanical advantages over others, but if properly operated they will all accomplish most of the work for which they are designed.

THE MAKING OF EMULSIONS

There is no doubt but that the modern mechanical means of making emulsions are far superior to the former methods of tank agitation, churning action, etc., for in such instances it was almost impossible to give the entire product the same treatment In a homogenizer or colloid mill, the entire mixture in the supply tank has to pass through under uniform conditions, which usually leads to a more homogeneous emulsion (i.e , the globules of oil split up to more or less uniform size) These may vary from about one-half micron up to as large as two microns in size, and still make a fair emulsion. It is well in making emulsions by such mechanical means for one to picture what takes place in the formation of the emulsion, bearing in mind that in oil-in-water emulsions there are three main types:

1. Where the emulsifying agent is an electrical charge on the oil particles, which is probably due to adsorption of the hydroxyl ions of the water by the oil particles In this form of emulsion the oil concentration must be very low, as the electrical charge is not sufficient for stabilizing emulsions in which the concentration is above small percentages.[10] The author's personal experience has been that the limit is at about 1½ to 2 per cent of oil concentration, and in some of these instances it is doubtful whether there was not a natural emulsifying agent present as an impurity.

2. Where the emulsifying agent is a water-soluble colloid, that is, peptized by the water, such as soap, gelatin, sulfonated oil, albumin, etc. In these types the oil concentration is sometimes increased up to over 70 per cent oil and the emulsions are more or less in a stable form.

3 Where the emulsifying agent is insoluble, or only slightly soluble in either phase In such an emulsion the very finely divided particles in the interface between the oil and water form the protective coating or sack about the oil globule. This material in such instances must be very finely dispersed and is probably adsorbed on the surface of the oil globule, thus preventing coalescence

Nordlund has shown that emulsification can take place in two

[10] Clayton, *op. cit*, p. 15; *also* Lewis, *Kolloid-Z*, 4, 211 (1909)

different ways. He illustrated it with mercury drops. He showed that emulsification can take place either by crushing the mercury drops or bursting the mercury lamellae. Svedberg [11] has explained this condition quite fully: "If we force water containing potassium citrate through a layer of mercury, very thin mercury films are produced when the water bubbles rise through the mercury. On bursting, the mercury lamellae give rise to extremely fine drops of mercury. Nordlund could actually, by having a very fine intense beam of light passing close to the mercury surface, observe the process, and could see how the lamellae exploded and formed clouds of mercury colloid. If, on the other hand, we eject mercury through a fine glass tube against a glass wall, under the same weak citrate solution, we get only a coarse emulsion. These considerations probably apply also in other emulsifying processes, but in cases where the interfacial surface tension is very low, the amount of energy required to form a fine drop is not very high and accordingly one would not expect a very striking difference between the two processes outlined above." Svedberg thereupon states that some of his experiments on the emulsification of oil confirm these conclusions.

FACTORS IN THE MAKING OF EMULSIONS

As previously mentioned, in dairy emulsions Nature has furnished the necessary emulsifying agents in the form of casein and lactalbumin, while in most other types of emulsions it is necessary to add the emulsifying agent. Most of the emulsifying agents added are gelatinous colloids but it is not necessary that these always be such, for anything that will go into the interface and make it sufficiently viscous, that is, form a protecting film, will give similar results. If enough of a fine powder is present in the interface, a plastic mass will be formed which will stabilize the emulsion, and it is not necessary that the emulsifying agents be in suspension. If these particles are properly adsorbed by the oil globule a condition is reached which will result in emulsification.

Specific gravity and viscosity are factors in some types of oil-in-water emulsion, as shown in experiments made by Seifritz,[12] who emulsified oil in water by the use of casein as a stabilizer. He found that by carefully regulating fractions of petroleum distillates, when the specific gravity was 0.820, fine stable oil-in-water types of emulsion could be obtained when the specific gravity was 0.828 they formed coarse and unstable oil-in-water emulsions. Those with specific gravity from 0.828 to 0.857 would not form emulsions at all. When the specific gravity was

[11] Svedberg, "Colloid Chemistry" (Wisconsin Lectures), Chemical Catalog Co., New York, 1924, p. 27.
[12] Seifritz, *J. Phys. Chem.*, 23, 587 (1925).

increased, however, from 0.857 to 0 869, the oil droplets were again formed into a coarse emulsion moderately stable, while those from 0.869 to 0 895 specific gravity and above formed fine stable emulsions of the water-in-oil type. These results are rather unusual and show a tendency to reverse the type of emulsion according to the specific gravity of the oil.

The statement is frequently made that if the viscosity or gravity of the oil is considerably increased, the emulsification is not so good. On the other hand, the author has made frequent emulsions where the specific gravity was almost that of water and it has been his experience that when this point is approached, the emulsions are, as a rule, more stable There is no great difference in specific gravity between the two phases, and this is a factor in favor of stability. While the author has not conducted the petroleum distillate experiments cited above, he has made numerous emulsions of mineral oil where the specific gravity varied from 0.87 to 0 90 without any tendency for the emulsion to reverse if the oil was less than 70 per cent; that is, he obtained the typical oil-in-water type of emulsion. In order to reverse it, it was necessary to use different types of emulsifying agent, according to the general rule, which is that the type of emulsion formed depends upon which phase the emulsifying agent is dispersed in. Water-soluble emulsifying agents promote the oil-in-water type of emulsion while oil-soluble emulsifying agents promote the water-in-oil type; or, as it is commonly stated in the case of soaps, a monovalent soap will make an oil-in-water type of emulsion while a bi- and tri-valent soap will make a water-in-oil type.

STABILITY OF EMULSIONS

When emulsions of oil in pure water are made, they will not be stable unless an emulsifying agent is added—that is, for emulsions where the oil concentration is over 2 per cent. Emulsions of oil in pure water having small proportions of oil are dependent upon the following: *a,* the interfacial tension tending to bring about coalescence of the globules whereby the total surface would be reduced; *b,* the Brownian movement tending towards collision of the globules, a factor operating against stability; and *c,* the electrical charge on the globules tending to repel them from each other on near approach, when these globules all carry a like charge.

Most of the work on emulsion stability relates to the influence of added electrolytes. When colloidal particles are coagulated under the influence of an electrolyte, globules adsorb oppositely charged ions so that their charges become neutralized Complete neutralization occurs at the isoelectric point, where the potential difference between the par-

ticles and the medium in which they are dispersed becomes zero. This can be demonstrated by passing an electric current through such an emulsion; it will be found that the particles will not then migrate to either electrode, while in the normal oil-in-water type of emulsion the particles carry negative charges and migrate to the positive pole. At the isoelectric point the emulsion is least stable

Hatschek [13] tried the addition of hydrochloric acid and sodium sulfate to effect coagulation or coalescence of emulsions. He found that at or near the isoelectric point the particles did coalesce, forming larger droplets, about 3 microns in diameter, but even this size of globule rises very slowly in the solution (about 2 cm in 48 hours). Ellis [14] has shown that the oil-in-water type of emulsion is more stable in the presence of a slight trace of alkali, such as a few drops of $N/1000$ sodium hydroxide, and least stable in the presence of aluminum chloride (0 00022 molar) He has also shown that it requires more of some of the other electrolytes to get the same condition, and cites the case of copper chloride (0 004 molar). Sodium chloride requires a larger quantity (0 16 molar). From the various proportions above cited one readily appreciates that as the positive charges present in the electrolyte are decreased from aluminum, with its three positive charges, to sodium, with its one positive charge, the quantities would, naturally, increase in order to neutralize the negatively charged particles on the oil globules and approach the isoelectric point Stability is improved where the slight trace of alkali is sodium or a monovalent alkali. The hydroxyl radical is probably adsorbed on the oil globule and assists in maintaining the difference in potential by maintaining the negative charge of the oil globule If the alkaline reaction has been brought about by the use of calcium hydroxide, the stability will not be improved. This is probably due to the fact that the calcium with its two charges offsets the effect desired

Powis [15] has shown that the conditions depend largely on the contact potential reached and that the zone of greatest instability is attained at ± 0.03 volt. In other words, within this range in difference of potential the effect is about the same and the charges are not effective until the potential difference is increased This potential was reached in the presence of the following millimolar proportions of electrolyte:

KCl	51 0
BaCl₂	1 9
AlCl₃	0 02
ThCl₄	0 007

[13] Hatschek, *Kolloid-Z* , 9, 159 (1911)
[14] Ellis, *Z. phys Chem* , 80, 597 (1912).
[15] Powis, *Z phys Chem.*, 89, 186 (1914)

When the concentrations given above were slightly increased, the oil globules took on a positive charge and became stable again, but under a condition not normal to the usual type of oil-in-water emulsion. Similar conditions are sometimes brought about by adding colloidal clay to an oil-in-water type of emulsion. If the emulsification has been brought about with the usual emulsifying agents, resulting in a negative charge on the oil globules, then when the clay is added, it is followed by coalescence and separating out of the emulsion, unless it is very carefully taken beyond the isoelectric point and given a positive charge. Under such conditions it is possible to have oil-in-water types of emulsion in which the particles carry a positive charge These are very rare, and it is more or less of an unstable condition Therefore, if one wishes to obtain an emulsion which will be permanent over a long period of time, an effort should be made to keep it slightly on the alkaline side. In commercial operation it is better to determine this by hydrogen-ion control, so that one may obtain the same dissociation of hydroxyl ions in each lot of emulsion made up The hydroxyl-ion concentration should be slightly over the neutral point of 7 0 Some commercial applications in emulsions require a pH of 8 0 so as to be very slightly on the alkaline side This has been found, in the past, to be excellent practice and is of great assistance.

CORRECTION OF EMULSION FORMULAS

In the preparation of emulsions, as well as in trying to locate causes of separation where some remedy must be applied, one must visualize the problem. It is of great assistance in correcting faulty emulsions to have some mental conception of how the emulsion is made. In order to get a clear picture of what apparently occurs in the making of emulsions, the author believes it is advisable to sketch this out in more detail so one may see at a glance what a great number of workers and research men in emulsion work believe really occurs. For purposes of illustration, we will classify the various phases of emulsion as follows: the two liquids we will call a and $b,$ and the film between the interface we will call c. According to Gibbs [10] it is most important that we consider the two surface tensions, that is, the one at the contact between a and c as well as the one at the contact between b and c. If the surface tension of the water phase is lower than that of the oil phase, the film in the interface will tend to curve so as to be convex on the water side and we have the tendency to emulsify oil in water. If, on the other hand, the surface tension of the oil phase is less than that of the water, the film will tend to curve, so as to be convex on the oil side, and we have the tendency to emulsify water in oil. Now

[10] Gibbs, "Scientific Papers," 1906, p 258

it is a question of the emulsifying agent added to the water phase or the emulsifying agent added to the oil phase which determines which way the film will bend In other words, if we wish to get an oil-in-water type of emulsion, we should strive to lower the surface tension of the water phase so as to make the film bend convex to the water. The phase with the greatest surface tension will have a tendency to contract into the smallest area which happens to be a sphere. As Briggs has stated, we get oil-in-water emulsions if the emulsifying agent at the interface is chiefly in the water phase, and water-in-oil emulsions if the emulsifying agent at the interface is chiefly in the oil phase.

Since the difference in surface tension brought about by emulsifying agents, as a rule, is not sufficient for one phase to peptize the other in this manner, it is usually necessary to break up the dispersed phase into fine drops by some mechanical means. This might be accomplished by agitation and various mechanical shaking devices, but the better practice seems to be by the use of homogenizers or colloid mills, for the reason that under such conditions the product is all uniformly treated and there is a more homogeneous splitting up than is accomplished by agitating or shaking methods. By such mechanical means the droplets can be split into small globules, as a rule about one-half micron in size, when the proper emulsifying agent is present. It is quite essential that the emulsifying agent added be one very carefully selected for the problem at hand. The machines will split this into a very fine white emulsion. While it is possible to get the same conditions through agitation, it is not always so reliable. To obtain this uniform splitting up, every particle in the emulsion should be subjected to the same identical conditions This is not possible in the case of tanks, where there may be dead spaces, or in shaking devices, which are more or less irregular in their method. It can be accomplished in a reliable way and the results duplicated from day to day either by the use of a proper pressure type of homogenizer or by several of the modern so-called colloid mills.

PHYSICAL ACTION OF THE EMULSIFYING AGENT

Clowes [17] found that sodium, potassium and lithium soaps emulsify oil in water, while magnesium, strontium, barium, iron and aluminum soaps emulsify water in oil. The soaps of the first series above mentioned contain monovalent metals, and are soluble in water, but not in oil. Those in the second series contain bi- and tri-valent metals and are soluble in oil but not in water. In other words, the alkali soaps are wetted more by water than by oil, and probably the surface tension is lower on the water side than on the oil side of the globules,

[17] Clowes, *J Phys Chem.*, **20**, 407 (1916).

so the film will bend convex to the water and concave to the oil, enveloping the oil globules, as the area of the inner surface of a sphere is less than that of the outer. Similar reasoning holds for the reversing of the emulsion by the other soaps mentioned, which are more soluble in the oil phase.

The above-stated facts are most important in obtaining stability, and are very frequently the cause of separations. As an illustration of this point take a case which came up fairly recently. A manufacturer was having trouble with separation of his emulsion and yet his formula apparently was proper. On investigation, it was found that he was shipping this emulsion in iron drums. Air was present, and the water being the outer phase, the air caused considerable rusting. Thus an iron salt thereupon entered the emulsion and had the tendency to reverse it. The separations were largely caused through this action. The author also recalls an experience of a few years ago. A manufacturer was making a disinfectant and the formula had been satisfactory for months when suddenly the product began to separate shortly after manufacture. The author found, upon investigation of this case, that the emulsion after manufacture was pumped into an iron storage tank. Upon examining this receptacle the sides were found to be coated with iron rust. This was getting into the product, causing one portion to go into the water-in-oil type, while the other portion was of the oil-in-water type. In other words, the manufacturer had an emulsion with three different zones. The solution of this problem was merely to change over to a glass-lined storage tank when the trouble apparently ceased. These cases are cited as typical. It seems necessary to elaborate on this point because it has caused trouble in commercial handling of emulsions, and the manufacturer should always bear in mind that monovalent soaps promote the oil-in-water type and the bi- and tri-valent soaps promote the reverse. This is a typical example where the theory applies very much to the practice. It brings out the point of the importance of the manufacturer having some basic ideas on emulsification so as to be able to eliminate such troubles.

If we make a typical emulsion using as an emulsifying agent sodium oleate (which, of course, is a monovalent soap), then on the addition of calcium chloride a certain point will be reached when the calcium concentration exceeds the chemical equivalent of the sodium, tending to reverse the emulsion. In other words, the two positive charges on the calcium would offset the negative charge on the surface of the dispersed oil globules, neutralize the electrical effect, and at the isoelectric point the emulsion would be in a very unstable condition. If, however, we continued the rapid addition of calcium chloride, it is possible to reverse this emulsion as demonstrated by Clowes.

It is very easy to demonstrate this fact through a diagram showing what we assume to take place under such conditions (Fig. 6).

A represents an oil-in-water type of emulsion where sodium oleate is used as the emulsifying agent, or one in which the sodium oleate is in excess so as to promote this type of emulsion. *B* represents a condition at the isoelectric point where we have the chemically equivalent proportions of sodium oleate and calcium oleate. *C* represents the reverse condition where the calcium oleate predominates, bending the film in the reverse direction, and encasing the water as previously described.
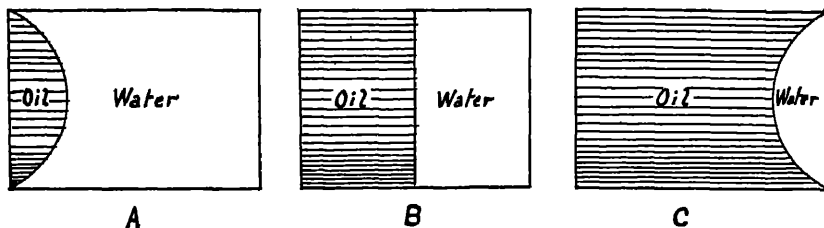
FIG 6.—Conditions at the Interface on Various Types of Emulsions.

If one can visualize this condition while working with emulsions, it will no doubt be of great assistance in correcting faults in the practical making of emulsions

THE WEDGE THEORY

Considerable investigation has been undertaken in recent years on the probable state of the film which divides the oil from the water in a typical emulsion. This has brought forward the recent development of the wedge theory of emulsification based on the orientation of the molecules at the interface. This work has been largely conducted by Hildebrand and Harkins.[18] One of the interesting phases of it is that the hypothesis demands that these films be one molecule thick or of similar dimensions (*see* p. 83). The theory is, in the author's opinion, a very logical one and is based upon the principle that the portion of the molecule which has more or less affinity for the water phase will be oriented in that direction, while that portion which has more affinity for the oil phase will be oriented in the direction of the oil droplet. For instance, in the case of a soap, the carboxyl group to which the metal is attached would be facing towards the water phase, while the hydrocarbon groups would be facing towards the oil phase. They would thus adjust themselves about the oil globule in an oil-in-water emulsion so that the molecules would form a sort

[18] Harkins, Davies and Clark, "Colloid Symposium Monograph," Vol 2, Chemical Catalog Co, New York, 1925, p 141.

of armor around the oil particle and take up a definite position of orientation. Of course, in an oil-in-water type of emulsion it is logical to assume that the oriented molecule of the emulsifying agent is largely in the water phase. The evidence does not always indicate that these films are just a molecule thick, for in some instances the membrane surrounding the dispersed drop is optically visible.

The wedge theory is not entirely new and it is found all through the literature [19] from about 1917 on. It has been hinted at by a great number of writers. It is a very difficult thing to prove positively but the hypothesis certainly appears to have some merit.

A very peculiar result came to the author's notice a few years ago while working with emulsions. He had occasion to finish an oil-in-water type of emulsion which had been passed through a homogenizer under fairly high pressure Upon completion of this work a microscopic examination was made and it was observed that the globules were quite uniform and averaged about one micron in size This emulsion was allowed to remain overnight and was examined the next day. One of the peculiar results was that the particles were down to about one-half micron in size, although the emulsion had been carefully put away after finishing the test the evening before. As this result was so unusual it was given some consideration and in trying to visualize what took place, the only theory of emulsions which would explain this was the orientation or wedge hypothesis. As an illustration, we know that in the building of an arch, the angle of the keystone of the arch determines the size. Now, if the molecules of the emulsifying agent happen to be of a wedge shape, it is reasonable to suppose that in orienting themselves about the oil globule, the keys did not just fit together. Some pressure was exerted through this orientation and the oil globules split up so as to accommodate the surplus molecules of the emulsifying agent. At least, this is one explanation which might be made of this unusual occurrence. The author inquired among a great number of his associates whether they ever observed such phenomena, and very recently one of his clients, who was visiting the laboratory, made the statement that he had had the same experience. It was agreed that the above was at least a plausible explanation.

We also know that in some instances in making emulsions, if there is a large excess of emulsifying agent the emulsions do not appear to be so uniform or so finely dispersed. This might be taken to the outer extreme in this case where the molecules did not have the opportunity to orient themselves properly. The author is not aware of anyone having done any great amount of research in emulsions who claims that orientation always takes place, for we know of cases where the

[19] Langmuir, *J. Am. Chem Soc*, **39**, 1848 (1917), *also* Harkins, Brown and Davies, *J Am. Chem. Soc.*, **39**, 354 (1917).

films are very thick and where they can even be changed from the state of spheres to flat needle-shaped globules without breaking the film, which would imply that these films are very tough and must be more than a molecule thick. Nevertheless, in certain types of emulsions and under ideal conditions, the evidence goes to point towards orientation of the emulsifying agent about the dispersed globules.

SEPARATION OF EMULSIONS

An oil-in-water type of emulsion when not properly made may decompose progressively. The free oil may come in contact with the films around the oil droplets and tend to bend these films in the opposite direction, thereby liberating additional oil due to the cracking of the films about other particles This is one way that we can picture an emulsion decomposing or breaking up progressively. There is also the possibility of the films about the oil globules cracking, due to sudden temperature changes and through period of ageing Of course, just what causes these films to crack or break and liberate the oil globules has not been definitely proven, but we do know that anything which destroys the film naturally destroys the emulsion. For instance, the addition of alcohol may absorb some of the hydroxyl radical from about the oil droplet or cut through the film due to its solvent action and so destroy the emulsion. In soap emulsions, for instance, acids readily destroy the film, liberating fatty acids from the soap and thereby breaking the emulsion Of course, in this instance, the fact that we are increasing the hydrogen-ion concentration is important. This, in turn, effects the adsorption of the negative ions. In any event, by attacking the emulsifying agent it is easy to break the emulsion. This may be done by the addition of electrolytes having strongly adsorbed positive ions, thereby neutralizing the negative charges, or by the addition of a substance which is mutually soluble in both phases of the emulsion, thus interfering with the separation of the two phases by the film However we view this, there is certainly no room for doubt that if we wish to break the emulsion, we must attack the film at the interface and if we wish to promote stability in the emulsion, we must keep the condition of electrical charges right for such stability to assure this film remaining intact This emphasizes the importance of hydrogen-ion control in the proper study of emulsions so as to keep the typical oil-in-water type of emulsion slightly on the alkaline side There are very few instances where the oil globules in such a type have a positive charge, and these instances are somewhat questionable, for generally speaking, they always carry a negative charge in a typical oil-in-water type.

The statement is frequently made that emulsions will not stand

freezing, and undoubtedly this is true in the majority of cases. Within the past three years the author has had occasion, however, to make mayonnaise dressings which were required to withstand freezing A number of such emulsions have been placed in a brine solution at —21° C. and allowed to remain there for periods of from six to eight hours; the emulsions were afterwards thawed out without showing any signs of breaking This process was developed for a manufacturer who was in trouble on account of the returning of mayonnaise shipments in winter. With this experience the author cannot, of course, make the statements that emulsions will not withstand freezing. In this instance they certainly did. Perhaps, if it were necessary, it might be possible to carry out similar ideas in other industries The author's emulsion work in other fields to date, however, has not required this.

VARIATIONS IN CONCENTRATION OF EMULSIONS

After various periods of standing the concentration in emulsions sometimes varies with the depth We commonly speak of this as the "creaming effect" Perrin[20] concluded that if emulsions could be made uniform, dilute emulsions would comply somewhat with the gas laws. He started with the supposition that if it were possible to obtain an emulsion in which the oil globules were all of uniform size, then the granules of such an emulsion should distribute themselves as a function of the height in the same manner as the molecules of a gas would when subject to the influence of gravity. For instance, the air at sea level is more dense than that upon the top of a mountain, and Perrin concluded that the granules of an emulsion may likewise vary in dilution or concentration at different depths; that is, vary at different heights from the lower layers, and the law of rarefaction would be similar to that of gases, or for the air in the atmosphere.

By fractional centrifuging Perrin was able to prepare a uniform suspension of gamboge in water with which he tested this hypothesis He found that with gamboge particles of 0.3 micron in diameter, a rise of 30 microns was sufficient to lower the concentration to about half its value, and he concluded that 30 microns in gamboge suspension is equivalent to 6 kilometers in the air. Other somewhat similar results were obtained by Zangger[21] for drops of mercury, and by Brillouin[22] for gamboge in glycerin solutions of high viscosity. Bancroft[23] points out that this cannot be true over any appreciable range

[20] Perrin, "Brownian Movement and Molecular Reality," 1910, p. 22 *See also* Bancroft, *op cit*, p 162, 163, 165.
[21] Zangger, *Kolloid-Z*, 7, 216 (1911)
[22] Brillouin, *Ann Chim Phys*, 27, 412 (1912).
[23] Bancroft, *op. cit.*, p. 163.

because it would mean that concentration would drop to one-billionth in a rise of about a millimeter. Hence, no colloidal solution would appear uniform. Burton [24] has suggested that the concentration increases with increasing depth only up to a certain value and then remains constant.

Of course, in emulsions where the oil is of lighter gravity than the water, the concentration of the oil phase would naturally be more in the upper layers of the emulsion after long standing and would decrease as samples from the lower layers are obtained. This is more true in cases of poorly made emulsions than in those which are fairly uniformly split up by mechanical means. If the proper emulsifying agent has been used and other conditions kept right, there will be very little difference in concentration, whether the sample is taken from the bottom or top layers of the emulsion. Such an emulsion, if properly made, should not show any water separation on the bottom nor the so-called creaming effect on the top For instance, with milk which has been homogenized and properly preserved so as not to decompose, it is impossible to obtain any such signs. We therefore strive in making emulsions to keep the conditions similar, and while, no doubt, there will be slight variation in concentration, as pointed out by Perrin, it should be so slight that for all practical purposes it would pass unnoticed.

A properly made emulsion is a poor conductor of heat, as noted by Pickering [25] It is possible to boil such an emulsion for several minutes, while the center remains at less than the boiling point. Such emulsions when kept in closed vessels are permanent for months. If allowed to come in contact with the air, they would, of course, form a skin or film over the surface, due somewhat to evaporation of the water phase at the surface. This causes a change in concentration at this point, which, in turn, brings about a condition of unstable equilibrium, due to the action of the electrolytes in the air, principally carbon dioxide, which is absorbed by the surface layer of the emulsion at temperatures below 15° C At lower temperatures this action is not so pronounced, probably due to the fact that we do not get such rapid evaporation at the surface. One can readily appreciate that emulsions should be kept from the air as much as possible when in storage. The container should be well filled and sealed.

COLOR IN EMULSIONS

A properly made emulsion should have an appearance similar to milk, that is, it should be very white, due to the fine splitting up of the oil droplets, regardless of the fact that a dark-colored oil might

[24] Burton, *Proc. Roy Soc.*, 100A, 414 (1921).
[25] Pickering, *J. Chem. Soc.*, 91, 2002 (1907).

be used When finely split up, these oil droplets have the property of scattering all the light and giving the emulsion a white appearance. The finer the droplets are split, the whiter the emulsion, as a general rule. Of course if it were possible to split the emulsion to sizes below two-tenths of a micron, this whitish appearance would decrease because of the fact that the oil droplets would then be split sufficiently fine so that they would be smaller than the distance between the wave lengths of some of the light rays, and the emulsion would begin to appear transparent It is not possible mechanically to split asphalt emulsions and other very dark-colored oils fine enough so that they become white in appearance They do shade off from the black color to light chocolate brown, indicating that if they were split more finely they would finally approach the white color, for the reasons above explained. Therefore, when making emulsions mechanically we know that when the discharge from the machines is a light color the microscope will always check back and prove that these particles are finely split. They are merely scattering the light and giving this white appearance

In the typical oil-in-water type of emulsion, where the indices of refraction of the two liquid phases are somewhat different, one gets the effect of a white emulsion The finer the oil globules are split the whiter the appearance until the outer zone of true colloidal dispersion is approached. Here it would begin to work towards transparency, but it is impossible to reach this zone by the usual mechanical methods. Holmes and Cameron [20] regulated the indices of refraction of the two liquid phases so as to have them practically equal, and by emulsifying glycerol in an acetone solution of nitrocellulose, to which benzene was added to regulate the indices of refraction, they were able to get various color effects. The emulsion at first was yellow, as viewed from the side, and blue by transmitted light. The addition of benzene changed the yellow to pink, while by transmitted light it became green; with the addition of benzene the pink was changed to lavender and then to a peacock blue If the indices of refraction are carefully regulated to be identical one can obtain a transparent emulsion. These color changes are sensitive to change in temperature.

In order to understand these color effects, comparison must be made with other similar effects brought about through other means For instance, if we have very fine particles suspended in a transparent solid, liquid or gas, they scatter blue light (presumably by refraction) more than they do red light; therefore, the mass appears red by transmitted light and blue by reflected light Skim milk is an instance, being distinctly ,bluish by reflected light and reddish by transmitted light. Tobacco smoke is another example, being blue by reflected

[20] Holmes, *J. Am. Chem. Soc.*, **44**, 71 (1922)

light and red by transmitted light. Bancroft [27] attributes the blue color of the sky to the light which is scattered by drops of liquid or particles of dust in the air, or even by the nitrogen and oxygen molecules themselves. He points out that the intensity of the color is due to the fact that we see it against the black background of infinite space. The sunset colors are due to light which is transmitted and not scattered From these comparisons one can readily appreciate why Holmes and Cameron obtained the various color effects in the emulsion above described.

THE FORMATION OF FOAM

In oil-in-water types of emulsion, where the globules of oil are coated with the viscous film containing water and with water as the outside phase, if the oil droplets are large they will rise to the surface or cause what we call creaming. The upper surface may consist of oil drops with their viscous coatings practically free from water. If these coatings have sufficient strength, coalescence will not follow for some days, and there will be a thick sort of scum on the surface. If we visualize these globules of oil replaced by air, we will have, of course, a mass of froth in which the bubbles will be of a very fine state of division. Hence, the conditions for formation of froth must be similar to those for the making of an emulsion.

Foaming is a sign of low surface tension, and as a rule when the addition of an emulsifying agent brings about excessive foaming we are likely to obtain a good emulsion. Hence, any substance which lowers surface tension sufficiently to bring about a fairly stable foam should be investigated as a possible emulsifying agent, due to this close relationship. Freundlich [28] concludes that a low vapor pressure in, conjunction with a low surface tension and high surface viscosity is essential to foam, and apparently this is the case where one is interested in a fairly permanent foam. To produce a foam it is essential that there be a distinct surface film; that is, that the concentration of the surface layer shall differ greatly from that in the concentration of the mass of the liquid. If this foam is to be fairly permanent, this surface film must be viscous, and when this foam cracks, the stabilizer about the air globules does not readily go back into the colloidal solution but is likely to remain as a precipitate There is apparently no reason why minute air bubbles cannot be emulsified in a liquid.[29] In other words, air emulsified in water is obtained instead of oil, provided the air bubbles are under proper pressure so as not to liberate themselves from

[27] Bancroft, *op. cit.,* p 248.
[28] Freundlich, "Kapillarchemie," Akademische Verlagsgesellschaft, Leipzig, 1909, p. 302.
[29] Bancroft, *op. cit.,* p. 366.

such condition. This may be a factor in bottled beverages where the sugar syrups with their flavorings are charged with carbonic acid gas, but what we are really getting is a very fine dispersion of the gas in the water phase. With a stabilizer or emulsifying agent present the gas bubbles can be entrapped in a similar state to that in an emulsion and thereby enclose surplus gas in the product considerably beyond the saturation point.

THE FLOTATION PROCESS

One of the commercial applications of a proper froth is its use in the flotation process. By this means sulfide ores may be separated from the siliceous gangue. It is really sedimentation up-side-down, for by adding a few tenths of a per cent of oil per ton of ore separated, a froth is formed. These minute droplets of oil are coated by the ore and bubbles of air are passed up through the mixture. These lift the ore particles to the surface. The oil globules evidently do not have any affinity for the siliceous matter, which settles. While the gravity of the silica and gangue is much lower than that of the ore, nevertheless the ore particles are lifted to the surface due to the attachment of the air bubbles. If there is no ore present, bubbles of air are formed, coated with a thin film of oil around which is the water in the outer phase, but the oil film is not viscous enough to form a suitable froth. When the ore is introduced into the oil-water interface, stabilization of the film is reached. In other words, the fine particles of sulfide ore form a coating about the air bubble, similar to that obtained with an oil-in-water type of emulsion when a finely dispersed product enters the interface. The froth resulting by this process is scraped off the surface. The process is used on a very extensive scale and is especially adaptable to sulfide ores. In this process a great variety of oils have been used and some of the blends give better results in such instances. One of the oils may spread over the surface and be a good frothing oil, while the second may assist in carrying the sulfide particles into the interface.

If the amount of air is not sufficient, the oil may cause the ore particles to flocculate and sink. On the other hand, if the amount of air is in excess of the proportion of the ore, the number of bubbles being thereby out of proportion, there is not sufficient ore to coat them. In such instances it is similar to the case of an emulsion—the air bubbles will coalesce. It seems to be essential that the fine particles of ore form an armor plate or protection for the air dispersion. Therefore, it is more than likely that when the flotation process is explained fully, the explanation will be brought about through paralleling the case with emulsification. The evidence seems to indicate that flotation is just

carrying one of the theories of emulsification into practical application on a large scale. Each year 70,000,000 tons of ore are handled in America by this process alone, and it is used very extensively throughout South America, Alaska and other mining sections. It has, in a great number of instances, replaced the cyanide process.

A great amount of experimenting has been done with the flotation process, and this is one instance where the practice is far in advance of the theory. In this country pine oil has been extensively used for this purpose, blended with mineral oils, and the recent addition of potassium xanthate has been of great assistance in this work. Recently it has been possible to work with other ores than the sulfide.

FIGHTING FIRE

Another recent application of the value of foam and froth is its use in fire fighting. It has proven very valuable for the extinguishing of oil fires. A heavy carbon dioxide froth is formed through the contact of acid aluminum sulfate and a solution of sodium bicarbonate. To the sodium bicarbonate solution is added some licorice root, which acts as a protective colloid about the gas bubbles when the sodium bicarbonate comes in contact with the solution of acid aluminum sulfate, thereby forming a heavy foam or froth. This goes over the surface of the oil, and, of course, extinguishes the flame by shutting off contact with the air. The carbon dioxide, while generating an atmosphere which would tend to put the flame out, nevertheless is not in sufficient quantity to replace all the oxygen in the vicinity, but the blanket effect of shutting off contact with the air is certainly effective.

While the above is not intended for a complete description of the flotation process nor for the method of fighting of oil fires, it is merely called to the reader's attention to show some of the extensive applications of the principles used in the making of an emulsion One cannot help but realize that the theories involved in the making of emulsions also extend to all other types of dispersions where a protecting film is necessary to offset coalescence or flocculation. There are almost unlimited applications of these processes to the various colloidal fields, and, in fact, to all cases where we are handling matter in a finely divided state.

Chapter XIII.

Dispersion of Solids and Liquids in Liquids.

METHODS OF PREPARING COLLOIDAL DISPERSIONS

A great number of methods have been devised for the preparation of colloidal dispersions in liquids, including chemical, electrical and mechanical methods. These dispersed systems can be classified, however, under two general headings: 1. Dispersion methods, which is the subdividing of coarse materials into fine particles; 2. Condensation methods, or the gathering of small particles, molecules or atoms together to form groups of colloidal size.

In the dispersion methods, the relative surface of the system is increased, while in condensation methods the relative surface is decreased due to the materials being brought together within a smaller boundary than before   A typical illustration of the condensation method is by electrical means   When a heavy electrical discharge is passed between metallic electrodes submerged in a liquid, the metal particles are torn off in an extremely fine state of division. When dispersion is brought about under such conditions, the small particles cannot exist in the original state in which they were dispersed but condense on each other so as to form particles of colloidal size. A great number of methods have been devised for preparing colloidal solutions of many of the most resistant metals in this way.

DISPERSION BY PEPTIZATION

Some substances have the power to increase the swelling action and eventually to bring about dispersion of colloids. This is known as peptization. The term, not a very popular one, was applied by Graham to the action of certain reagents on colloids and is evidently derived from its analogy to the digestive action of pepsin. In the case of the action of pepsin on boiled white of egg, we are dealing with a process of hydrolysis which results in the transformation of the insoluble compounds into products possessing true solubility. Peptization is disintegration by chemical instead of mechanical or electrical methods. It is understood to-day to mean the diminution of the size of the aggregates and is, therefore, the reverse of flocculation. This solvent or peptizing action is applicable to all colloids, but is more marked with those that are insoluble in water   Thus, casein is peptized by alkaline

substances such as caustic soda, sodium carbonate, borax, sodium phosphate, etc. Gelatin is peptized by acids, Prussian blue by oxalic acid, fatty oils by alkalis. Glue, gelatin, soap, gums, etc, are not really soluble in water; they are in reality peptized by water, that is to say, subdivided into particles larger than molecules.

Peptizing agents assist in all grinding processes. For instance, in grinding, very fine particles are probably formed which again aggregate, while grinding in the presence of alkalis or other peptizing agents may bring about a loosening of the bonds between the primary particles. A typical example of this is pointed out by Svedberg. The Austrian engineer Kuzel invented a dispersion process in which he powdered very fine metals and treated them alternately with acid and alkali solutions and then with pure water. In this way he produced sols of various metals These were coagulated and used in the making of filaments for electric lamps. The tungsten filament, of course, has since replaced this.

Other solid substances have been ground by various types of grinders to a state where they were sufficiently fine to be classified as colloidal. Metallic inks can be made by grinding very fine powders in the presence of honey, and carbon inks by grinding with zinc, but, in such work, it is necessary to have a stabilizer present to avoid flocculation Graphite can be deflocculated by the colloid mill and dispersed with tannin which acts as a protective colloid.

It should be kept in mind that when substances are dispersed in the presence of gelatin or some other stabilizer, the substance dispersed does not necessarily have the same properties as would be possessed if it were in powdered form, for the protective colloid or stabilizer in order to function must form a film about each fine group of particles. This may considerably alter its properties, depending largely upon the nature of the substance dispersed

The size of the particles of solids dispersed in liquids varies greatly, some being below the limit of the ultramicroscope, while others may be readily seen with fairly low power of the ordinary microscope. This variation in size might be demonstrated by sulfur. If sulfur is precipitated by the action of hydrogen sulfide in an aqueous solution of sulfur dioxide, it is found to yield aggregates varying greatly in size The same is true of any other sol dispersed in a liquid.

Variation in Particle Size

Blyth, Martin and Tongue [1] state that there is a definite law governing particle size in fine grinding, especially in crystalline substances.

[1] Blyth, Martin and Tongue, *Nature,* 111, 842 (1923) ; *also* Bancroft, "Applied Colloid Chemistry," p. 213.

They cite the case of standard sand, which is as follows: "The rate of increase of the number with decrease of diameter of particles present at any given size is proportional to the number of particles of that size. It is therefore possible to calculate the number of particles of any given diameter without going through the laborious process of sieving. The law is probably the expression of the fact that crystals have a definite and fixed structure. Consequently, they break up when subjected to percussion, or pressure, in a regular and definite matter, which follows a definite mathematical law when the number of particles considered is sufficiently numerous to allow of the application of the law of probability." The above statement, of course, applies to solids and dry grinding, but it has been learned, through comparison of smoke and other dispersions in air or aerosols, that if sufficiently finely divided, they very closely follow the laws of fine dispersion in liquids, and must be considered. The fact must not be overlooked that as particles of matter become reduced in size, their surface becomes correspondingly greater. Therefore, the degree of dispersion and the increase in surface area is enormous in proportion, and such products have higher adsorptive power and chemical activity than the material in its usual form.

It might be well to add that the densest mixtures occur with particles of different sizes They are then more readily packed and a great amount of the void space is taken advantage of in such packing This fact is taken advantage of in all concrete mixtures where it is desired to obtain the maximum density in the mix.

If spheres of equal size are piled in a cubical form (in other words, packed within a box) there would be, theoretically, about 48 per cent of voids regardless of the diameter of the spheres, provided they were all equal in diameter. On the other hand, if the spheres are piled so that each one rests equally on four other spheres in the layer below, a maximum of hexagonal piling is obtained. This gives the lowest percentage of voids possible in piling spheres of equal size. In this instance, the void space is theoretically about 26 per cent When the spheres are of different sizes the void spaces can be decreased enormously. However, if the small particles have adsorbed air cushions about them so that they do not actually come in contact, the percentage of voids will increase enormously as the size of the particles is decreased. This is the condition encountered with fine powders, regardless of the fact that they are not perfect spheres. "Moist sand occupies more space and weighs less per cubic foot than dry sand" [2] for the reason that a film of water coats each grain of sand and separates it from the adjacent ones, and, as very fine sand has a large number of grains and therefore more surface area, the addition of water will cause increase in bulk to a much greater

[2] Bancroft, *op cit.,* p. 188.

extent than with coarse sand.[3] This is of considerable interest when considering' dispersion of such materials into liquids, and has important bearing on the viscosity or plasticity of the mixture after the dispersion

SIMILARITY OF COLLOIDAL DISPERSIONS

There is a great similarity to the behavior of fine dispersions of liquids in liquids and solids in liquids. Also, the work of Donnan[4] on neutral oil emulsions shows that there is a close similarity between such mechanical emulsions and colloidal suspensions In each the particles carry an electrical charge of similar order and magnitude, that is, the potential differences are very similar and the conditions for stability under the action of adsorbed ions are similar. While it is perfectly true that two small drops of pure liquid will coalesce easily to form a larger drop, in the case of small divisions of solid matter our experience has been the other way, yet finely divided solids behave like finely divided liquids in a great many respects. A very finely divided powder has a higher vapor pressure, a lower melting point and a greater solubility than the same substance in a more coarsely crystalline form.[5] This parallelism is so close in many respects that one is liable to wonder at the apparent failure of the solid particles to coalesce when in a finely divided state. The reason may be that conditions are not right for them to coalesce; this does not in any way disprove the theory that fine dispersion of matter, whether in a solid liquid or state, is not similar For instance, Bennett[6] has pointed out that if copper is precipitated on copper electrolytically, a mass is produced which does not differ greatly from that obtained in casting copper. That is, successive layers of copper when plated out coalesce to a uniform mass. This does not occur in the case of nickel plating unless special precautions are taken. The reason for this is, probably, that the original nickel first plated out had an oxide film over the surface and did not really come in contact with the nickel on the electrode.

If a china plate is broken into two pieces without chipping so that the two broken parts fit together again perfectly, they will not, of course, cohere again. This is due to the fact that a film of condensed air, which acts as sort of a cushion, keeps the parts from actually coming in contact. However, if it were possible to do this under a perfect vacuum, the particles would probably coalesce and the plate would be as good as new. Of course, to do this, would mean removing all air, which is absolutely impossible, but, theoretically, that is what should happen. Every

[3] Taylor and Thompson, "Plain and Reinforced Concrete," John Wiley & Sons, New York, 1912, p. 176.
[4] Donnan, *Z phys. Chem*, **46**, 197 (1903).
[5] Ostwald, *Z. phys Chem.*, **35**, 495 (1900).
[6] Bennett, *J. Phys. Chem.*, **16**, 294 (1912).

chemist knows that it is easy to make two glass rods unite at a temperature at which they are still very viscous, when it is doubtful if the glass is really in a liquid state.[7] One can understand why it is so essential in soldering or brazing metals that the surfaces be absolutely clean, so as to do away with all grease film. The similarity between the actions of fine dispersions of solids and those of liquids is so close that it is believed that the reason we do not get coalescence of small particles when in the so-called solid state is (*a*) because we have not gone far enough in our experiments; (*b*) the right conditions have not been obtained, and (*c*) matter in this finely divided state is almost identical.

In a homogeneous mass such as a liquid, if drops of similar liquid come in contact with the mass or body of this liquid, they coalesce and help to increase the contents of the mass For instance, if we have an oil and break it into drops, and these are all of the same material, they will, of course, coalesce again when they come in contact and re-form what we would call a homogeneous mass. If there is some foreign substance present, however, or an impurity picked up in the product, this may form, or assist in forming, a film, so that these particles cannot coalesce This is what occurs in the case of emulsification, but it also applies in mixing solids, gases, etc. As a typical illustration, let us take a case of welding For union to take place between two surfaces of a metal it is essential that they should not be covered with any infusible matter, for instance, scale, due to oxidation, which might form when heating the iron to a welding temperature Due to the fact that this does occur in the raising of the temperature in welding operations, this scale may be converted into a fusible and liquid silicate by throwing a little sand over it. The welding will then be effective, for the silicate will be squeezed out during the operation and clean metallic surfaces brought together.[8]

Copper in a finely divided state will coalesce and form a larger mass or solid body when submitted to great pressure, and, in fact, Ozann [9] has made copper medals using this principle, so we see that this principle of coalescence follows to a great extent all the way through, provided there are no impurities or other conditions to form a film foreign to the product, and one to which it will not bond or adhere.

Coalescence and Flocculation

Coalescence of liquids or flocculation of solids is brought about in liquid dispersions through sudden jar or vibration, or through the action of electrolytes, temperature changes, etc Also in the dispersion of fine

[7] Bancroft, "Applied Colloid Chemistry," 2nd ed., McGraw-Hill Book Co, New York, 1926, p. 208
[8] Percy, "Metallurgy of Iron and Steel," 1884, p. 6
[9] Tammann, *Ann. Phys*, 18, 856 (1905).

metallic oxides, etc, by the use of an electrical arc or discharge under water, it is believed that these particles when first dispersed very closely approach the molecular state, but that condensation quickly follows, and therefore, when such particles are observed under the ultramicroscope and classified as in the colloidal state, they have previously been in a finer state of division   Condensation is necessary before they are even in the range of identification by use of the ultramicroscope.

OTHER FACTORS PERTAINING TO STABILITY

The investigations on the stability of dispersoids carried out over the past thirty years, especially since those of Hardy,[10] have shown that the electrical charge of particles is most important in preventing their flocculation or coagulation, such coagulation taking place, as a rule, when these charges are removed.[11]   The particles repel each other when they all contain the same charge, hence, do not approach sufficiently close to each other to be attracted by each other, that is, to enter the sphere of attraction.   However, if a particle has an abnormally great velocity, due to excessive Brownian movement, it might be shot through the field of repulsion into the sphere of attraction of the other particle.   The mean velocity of the particles is governed by the temperature, but all particles of the same size will not necessarily have the same velocity   The electric charge rules the probability of adherence but not that of collision.   Svedberg [12] has pointed out that electrolytes affect the charge of the particles but do not alter their Brownian movement, and as long as the particles do not flocculate they will remain in suspension.

The action of protective colloids, such as gelatin, is to affect the probability of adhesion.   A protective action can be brought about, however, by other substances than those purposely added as protective colloids   For instance, water molecules adhering to the particles, and thus forming an aqueous envelope around each particle, will exercise a considerable influence on the probability of adhesion or coalescence.

The rate of coagulation of particles that are not totally discharged has been investigated by von Smuluchowski [13]   The electrical charge remaining will decrease the probability of adhesion.   The sphere o' attraction will be smaller and it is possible that there is no attraction left   This all depends upon the quantity of the charge on the particles

Both Ehrenhaft and DeBroglie [14] find that silver particles suspended in air are charged   By measuring the velocity impressed on their

[10] Hardy, *Z phys. Chem.*, 33, 385 (1900)
[11] Powis, *Z phys Chem*, 82, 186 (1915)
[12] Svedberg, *Acta. Reg Soc*, 2 Nr 153, *also* H Kruyt, in Alexander's "Colloid Chemistry," Vol 1, Chemical Catalog Co, New York, 1926, p 306.
[13] Von Smuluchowski, *Kolloid-Z.*, 21, 96 (1917).
[14] DeBroglie, *Compt. rend*, 146, 624, 1010 (1908), 148, 1315 (1909)

through a known electrical field they have measured the charges. Wells and Gerke [15] measured the velocity of smoke particles in an electrical field The particles may be held in suspension by having sufficient electrical field developed to offset the charge on the particles, or in other words, they can be held in electrical balance and from this particle size can be determined.

EFFECT OF LIGHT ON STABILITY

There is no doubt but that colloidal dispersions, and even substances in solution, are subject to great changes by the action of light. It is claimed that solutions exposed to blue radiations are more rapidly precipitated than those left in the dark, and that solutions exposed to active red radiations are not so sensitive to the action of such light. In other words, the chemical activity is retarded as the long wave lengths of the red are approached It has been a long-established practice of pharmacists to use reddish-brown bottles for sensitive solutions, and these doubtless are better for the purpose than blue ones.[16] For emulsions and other dispersions, there is very little doubt but that blue bottles should be avoided when the product is subject to long periods of storage where it is exposed to excessive light. Emulsions and colloidal dispersions at best should not be subjected to any more severity in treatment than is necessary. After all, the so-called colloidal state is not a stable condition under all circumstances, and as long as these facts are known, it is most advisable in the packing of products of this sort not to endanger the preparation.

The effect of change of temperature on the stability of colloidal solutions is most important. Raising the temperature as a rule increases the peptizing action of the solvent, and of course increases the stability. On the other hand, it may decrease the adsorption of the stabilizing ion, thus making the dispersion less stable. This second factor is very important with colloidal solutions which are stabilized by an adsorbed ion. Albumin solutions coagulate on heating, as does casein, and when a solution is frozen we have the possibility of colloidal agglomeration. In such an instance the colloidal solution will not re-form on melting the mass. In the presence of peptizing agents, however, this precipitation might be reversible. An illustration of this point is the instance cited in Chapter XII of a mayonnaise dressing which will withstand freezing for a period of fourteen hours and can be thawed out without breaking the emulsion. This is entirely a matter of proper protecting agents.

[15] Wells and Gerke, *J. Am. Chem. Soc.*, 41, 312 (1919).
[16] Audubert, in Alexander's "Colloid Chemistry," Vol. 1, p. 367.

SOME OTHER PROPERTIES OF COLLOIDS

In discussing the physical properties of colloids, there is the matter of so-called reversible and irreversible colloids For instance, when a so-called solution of a colloid is heated or evaporated, the colloid either remains unchanged or becomes insoluble. Gelatin will again dissolve while albumin after heating will not dissolve; hence the two types of colloids. In these examples, however, it must be remembered that gelatin, if heated sufficiently, will not go back into so-called solution, and also if albumin is taken down to dryness with low temperatures, it will go into solution again. Thus, in the above two cases, it is difficult to class one or the other as a reversible colloid. Under the right conditions a great number of colloids can be put back into so-called solution. Take an example of casein, which is ordinarily insoluble in water but with the aid of a slight amount of alkali is peptized It can then be dried under proper conditions and again put back into so-called solution. The casein is carried into apparent solution by the use of the alkali Indicators in these protein solutions are usually unreliable in the presence of proteins Hence, in determining the hydrogen-ion concentration, this must be considered; it is probably due to the adsorption of the indicators

Precipitation of colloids by electrolytes is usually an irreversible phenomenon The colloidal particles clot, forming a precipitate, which as a rule will not go back into the colloidal state. There are exceptions however, to this rule, such as a gold sol which when deposited by electrical means can be returned to the water phase as the original homogeneous sol. Where proteins have lost their property to return to a so-called colloidal solution, it is sometimes spoken of as denaturation. This may be brought about in the case of proteins by starch, action of sunlight, drying at elevated temperatures, action of acids, etc Any change in the properties of a colloidal dispersion whereby it will not return to its original sol, whether physical or chemical, is termed denaturation.

If a precipitation is brought about in a colloidal solution by the addition of an agglomerating agent, this precipitate may go back into apparent solution if such agglomerating agent is washed out. The colloidal solution will not be obtained again, however, if it is impossible to wash out the coagulating agent unless a peptizing agent be added to offset the precipitating agent.[17] In this case, it may not be necessary to wash out the precipitating agent, provided there is sufficient peptizing agent present to offset this effect. The peptization of silicic acid by caustic soda and of Prussian blue by oxalic acid or potassium oxalate are illustrations of this The washing action of soap is in fact the

[17] Abegg and Von Schroeder. *Kolloid-Z.,* 2, 85 (1907).

peptization of dirt adsorbed on the skin or fabric.[18] We say that the soap is a good emulsifying agent It forms an emulsion with the fatty substances, oils, etc., thereby removing the dirt, which might be classified as peptization because the particles are subdivided and dispersed by the action of soap.

This question of reversible and irreversible colloids should have further study before making this dividing line The structure of colloids is not well understood, and it appears that the reversibility of a colloid is largely a matter of the conditions present.

[18] Barry, *J. Soc. Dyers and Colourists,* **39,** 22 (1923)

Chapter XIV.

The Colloid Mill and Some of Its Applications.

Some years ago inventors busied themselves with the question of dispersing solid hydrocarbons into oil for the making of concentrated liquid fuels, and while frequent references may be found (in patent specifications of the time) to "high-speed mills," details seem to be lacking on such machines in some cases   Like all new developments where the manufacturer decides that a definite type of equipment should be used, this work was carried to excess. One optimistic colloidal fuel inventor tried to use a machine having a linear speed of 1,000 meters per second, which, of course, is far beyond mechanical limits. Even the alloys and materials that are available today could not withstand such strain. This and other prior dispersion mill work, however, was of great benefit, for it started people thinking along the line of mechanical dispersion by the use of high peripheral speeds, which ultimately resulted in the development of the modern so-called colloid or dispersion mill.

Von Weimarn, the Russian colloid chemist, stated in 1910 that he believed it was possible to make so-called colloidal dispersions by mechanical means. He proposed a shearing action and stated that it was necessary, and very important, to have present some stabilizer in order to protect the particles after dispersion and prevent flocculation [1] Apparently, from the early literature, Von Weimarn is the one entitled to the credit for an early publication of a conception of the colloid mill.[2] Unfortunately, a great amount of his work was published in the Russian language, and very few of our scientists were able to read it at the time There was a Russian engineer by the name of Plauson in Hamburg, however, who developed a particular form of the so-called colloid mill. He applied for patents [3] on it in the United States in 1921. At the time, this received wide publicity in various chemical journals, whereas Von Weimarn's early work, and his recent statement that he built his first colloid mill in 1912, had not received such notice. So, while Plauson was among the early investigators to work with so-called colloid mills, he apparently was not the originator of this idea.

It is unfortunate that, when the first articles pertaining to the Plauson mill were published, it was called a colloid mill   This, apparently,

[1] Von Weimarn, "Grundzeuge der Dispersoid Chemie," Verlag von Theodor Steinkopf, Dresden, 1910, p. 82.
[2] Von Weimarn, *J. Russ Chem. Soc*, 38, 466, 470 (1906), 39, 619 (1907).
[3] Plauson, U. S. Pat. 1,500,845.

is a misnomer; for, as has been emphasized from time to time throughout this book, such mills do not disperse to the true colloidal state. As a result of the wide publicity given to this equipment it is very difficult at this late date to change the term applied to it. Therefore, manufacturers of such mills, today, usually designate them as colloid mills. This has a tendency, of course, to create the impression, especially with the layman, that they really break matter down to the colloidal state. Some people even have the impression that they break down to the molecular state, which, of course, is absurd. The so-called colloid mill does not, as a rule, accomplish any grinding action, nor does it disperse in most instances to anywhere near a true colloidal state.[4] If such mills did accomplish this function, their present wide application would be greatly curbed, for if this were possible, the colloid mill would fail to function in a satisfactory manner in the dispersion of pigments, which at present is one of their greatest applications. If such mills, for instance, could disperse to a sufficiently fine state of division as to be classified within the colloidal zone it would mean that the diameter of particles would be less than the wave length of light.[5] The product would approach transparency, and the hiding or covering power of the pigment would vanish.

To be more explicit, in the fine dispersion of pigments and coloring matters in a vehicle in which they are insoluble, the hiding or covering power of such pigment is increased, as the particle size decreases, only until the outside limit of the so-called true colloidal zone is approached With a great number of pigments, after dispersion below a particle size of 0.8μ the hiding power starts to decrease, and it is not desirable to go beyond this limit It is not the intention to create the impression that the so-called colloid mill will even disperse to this degree of fineness of particle size. It will, under some conditions, give dispersion of pigments or coloring matters down to particle sizes of about $500 \mu\mu$ but these are not common. A large number of the fine crystalline substances are not very securely bound in their so-called lattice structure. In such instances the colloid mill may tear apart the crystals into a finer state of division and thereby bring about a suspension of such particles in a liquid or vehicle. But this is not real grinding.

DEFLOCCULATION AND DISPERSION

What the colloid mill really does is to deflocculate and, with a great number of substances, this is all that is necessary. This point might be illustrated with the dispersion of zinc oxide It is well-known that when such substance is first manufactured it is in a very finely divided state— what might, for commercial purposes, be classed as a colloidal state. In the packing of this product it groups or bonds together, so that when

[4] Von Weimarn, *Z. Chem. Ind Koll.,* 7, 155-157 (1910)
[5] Note: Yellow Light about 600 $\mu\mu$

the paint manufacturer uses it, all that is necessary is to deflocculate it in the presence of some vehicle. This is where the colloid mill is of value, for by dispersion through such a mill it is possible to obtain intimate contact of the vehicle with the small individual particles of the oxide, eliminate the air cushions brought about through adsorption, and replace these with direct contact of the vehicle with the power, in other words, increase its wetting power. Once these particles are deflocculated and are well wetted by the vehicle the dispersion is satisfactory for commercial application.

This statement also covers a great number of other instances where it is sometimes said that the product is ground One can readily prove this point by attempting to disperse carborundum or fused silica, where real grinding or disintegration would be necessary

It is hoped that this statement will help to clarify the situation and will emphasize the point to prospective users, that if it is a case of deflocculating, the colloid mill may be of value to them, as it has proven to a great number of manufacturers. If it is a grinding problem, where it is necessary to really disintegrate or grind, no colloid mill has as yet been built which will do such work. Of course, as time goes on, it may be that it will be made possible to really grind by use of a colloid mill of the continuous type From present evidence and study of the matter, however, the author is of the impression that in order to accomplish this it will be necessary to have enormous peripheral speeds, much beyond the mechanical limits of the continuous types of mill at the present time. The above facts, however, have not handicapped the progress of the colloid mill, which has found wide application throughout the chemical industry in various fields of operation.

If one will give a few minutes' thought to what would really happen if it were possible to grind down to the true molecular state of matter, the author believes it will be realized that in the majority of instances this is not desirable—at least in most commercial applications. First, take matter in the solid state and grind it by the method known as dry grinding, and assume that this could be ground as fine as desired. One would find that at a definite degree of fineness the vapor pressure would become sufficiently high so that the whole of the solid would vaporize. Again, if this were possible, our knowledge of flocculation and condensation leads us to believe that the material would immediately precipitate out as coarser aggregates or crystals.

Of course, in dispersion by colloid mills there must always be a liquid present, for such mills will not function except in the presence of some liquid Their principal action is based entirely on a so-called hydraulic shearing effect; hence, they obviously must have a liquid in which to accomplish their mission Now, if it were possible to grind a solid to the molecular state in the presence of a liquid, such solid

would become more soluble the finer its dispersion in the liquid. Eventually it would reach a particle size sufficiently small to be in a molecular state, or in what is known as true solution. This would probably act in a manner similar to the hypothetical case above cited, that is, the small molecular particles would again re-precipitate in groups.

For the reasons cited above this author believes it would be far better if the colloid mill were termed, or referred to, as a dispersion mill, or perhaps, a homogenizer, for it has a tendency to make the product appear more homogeneous. The difficulty encountered in designating such equipment as a homogenizer, however, is that this name will confuse the prospective user. It is liable to create the impression that it is similar to the old pressure-type homogenizer. The modern so-called colloid mill is far in advance of such equipment for most uses. Therefore, in using the term colloid mill this author wishes to make it clear that a great number object to designating this equipment as such. It is hoped, however, in time to correct the false impression and that eventually such machines will be called dispersion mills, a term which gives a clearer interpretation of the real functions of the machine.

Fig 7.—Original Type of Plauson Colloid Mill (described on page 152).

THE PLAUSON MILL

The Plauson colloid mill which created a sensation about eight years ago, is not upon the market today, at least not in the United States. The expectations for the mill were not fulfilled, largely for the reason that excessive horsepower was necessary. It therefore was not very successful on a plant scale. Another drawback was that it was intermittent in its operation. Regardless of these facts, the ultimate results accomplished with these machines seemed to be excellent, but the machine never became popular. Modifications, based on the principles of dispersion by hydraulic means, have come into great prominence in the last few years. These modifications are based on continuous operation, and far less consumption of horsepower.

THE SHEARING ACTION OF THE COLLOID MILL

A few words as to the distinctive methods of obtaining the hydraulic shearing forces in the colloid mill may be of interest. In the Plauson machine it was generally understood that a combination of shearing stresses and impact forces effected the dispersion, the revolving blades leaving and reentering the space between adjacent fixed blades with such rapidity as to impart sufficient hammering action on the particles dispersed.

The dispersion in all the various types of so-called colloid mills is due to hydraulic forces. In the film type of mill, wherein a film of liquid is sheared under pressure like a solid, the particles in line of shear become dispersed. In this type, the principles involved are apparently an adhesion of a certain portion of the liquid to the rotor and another portion to the stator, which causes a lamination or tearing action upon the particles in between In other words, there are a series of film surfaces, one tearing the other, by the principle of hydraulic shearing action. In the smooth surface film-type mill, where discs are rotated in opposite directions, a similar effect is produced. This

FIG 8—Modification of Plauson Mill (English type). Described on page 154.

result was brought about in a modification of the Plauson machine, sometimes spoken of as the English Plauson, in which two smooth discs rotate in opposite directions, and the product is fed through the axis of the machine. This type has been on the market in England for several years but apparently has not been popular in this country, at least to the present writing. The smooth surface film types of machine used in the United States have been based more on the truncated cone rotating in a similarly truncated stator; or the type in which the confining film is so shaped that it does not evacuate the space by its own inertia; or that in

which the rotating shaft is in a horizontal position. Such machines, as a rule, give a longer period of time on the dispersion surfaces, due to delayed action in the horizontal type.

<div align="center">VARIOUS TYPES OF COLLOID MILL</div>

In the smooth-surface or film type of mill, in which the liquid adheres with great tenacity to the relatively flat moving surfaces, there are two divisions· 1, those in which the liquid is propelled through a gap by the centrifugal forces acting upon the material forming the film, including machines having the working surfaces in the form of discs or flattish truncated cones diverging from the ingress end, 2, those in which the surfaces confining the film are so shaped that such film does not tend to evacuate the space by its own inertia or in which it actually tries to work back to the feed space. Both modifications of the second class are incorporated in the horizontal shaft type of colloid mill.

In the roughened surface type of colloid mill there are two divisions· first, those in which the rotor consists of a series of grooves rotating on a horizontal axis enclosed by a stator which also has grooved surfaces This machine brings forward other hydraulic effects than those obtained in a smooth-surface type There is a scissors action in combination with the hydraulic shear which is brought about through eddy currents formed in the grooves. Due to relative change in position, such currents are constantly subjected to a chopping action in conjunction with a resultant force brought about through counter-pressure while the product is passing through the machine. The second type includes those which consist of flattened discs with lugs alternating on the two plates. The product is fed through the axis and the lugged plates rotate in opposite directions which result in a hammering action somewhat similar to that of the Plauson mill but with the advantage of being a continuous type.

THE SMOOTH-SURFACE TYPE

The principles involved in both divisions of the smooth-surface type of continuous film mill are similar and are based on fundamental hydraulic phenomena In addition to considering the adhesion of liquid to the rotor and to the stator, which causes a laminating and shearing action of the intermediate layer of liquid (or what is usually spoken of as the lamination) the phenomenon of liquid rigidity should be kept in mind when such lamination takes place at high speed on the film subject to this treatment. The force of this action applied to the shearing will be realized when it is recalled that it is impossible to even pass a sword blade through a high-pressure jet of water. Its action is similar to that of a solid mass Such shearing action is terrific in a colloid mill of proper design with a peripheral speed of at least two miles per minute (10,560 feet). In the presence of a solid and the proper amount of

liquid so that the liquid acts as a carrier for the solids, the solid particles are subjected to severe shearing action which is sufficient to cause deflocculation and dispersion.

In order to give additional shearing action, attempts have been made to replace the rotor and stator with two discs rotating in opposite directions. It is claimed that by so doing the peripheral speed is increased, that is, that the shearing action is greatly improved. Such a type of mill has been used abroad for the past five years, but apparently has not met with great success in this country. It has been suggested that perhaps the effect of shearing is nullified or offset and that instead of obtaining additional shearing action, there is less real shearing by this method. Various modifications of this rotating disc idea are now being placed upon the market. It is too soon to prophecy as to whether any real advantage will be gained, as these mills have not as yet had sufficient testing to establish this fact positively in actual commercial practice There is a possibility, with such thin films of liquid as are necessary for proper dispersion, that by carrying out the idea of rotation of two discs in opposite directions, such film is not of sufficient thickness for one disc not to offset the effect of the other to a great extent. Such units would also require two separate motors or pulleys, so one would expect the horsepower to increase considerably. The principle of high speed of the rotor in close approximation with the stator is being used extensively in commercial operations and has proven its value over several years now. Therefore, it will be necessary for the principle of rotation in opposite directions to have a more thorough trial in the case of smooth surface film mills before making a definite statement for or against such principles.

In order to obtain a sufficiently finely dispersed condition, many substances require varying amounts of treatment. The treating time, or delay action while passing through a colloid mill, can be varied somewhat on certain types, and while this is only a fraction of a second, it is readily appreciated that this means several hundred additional feet of treating action which frequently is an important factor in hydraulic shearing, especially on materials that are rather difficult to disperse Small additions of proper dispersion agents serve to assist greatly in making fine dispersions in addition to acting as protective colloids, thereby accelerating the process Cases frequently occur where materials cannot be dispersed through a colloid mill in the presence of water without the addition of dispersing agents of the emulsoid type Such agents perform two functions, namely, the protection of the dispersoid, and the lowering of the surface tension of the liquid. There are numerous instances where a slight quantity of peptizing agent will be of great assistance in making of proper dispersion and in treatment of various materials.

THE VERTICAL SMOOTH-SURFACE MILL

The first type of smooth-surface continuous film mill includes machines having the working surfaces in the form of flattened truncated cones diverging from the ingress end. A cross-sectional cut of a typical machine of this group is shown in Figure 9. It will be noted that the product enters through the bottom and is carried up over the dispersing surfaces by the action of a rotor running at very high speed. Because of the slope on the rotor, which is at an angle of approximately 45°,
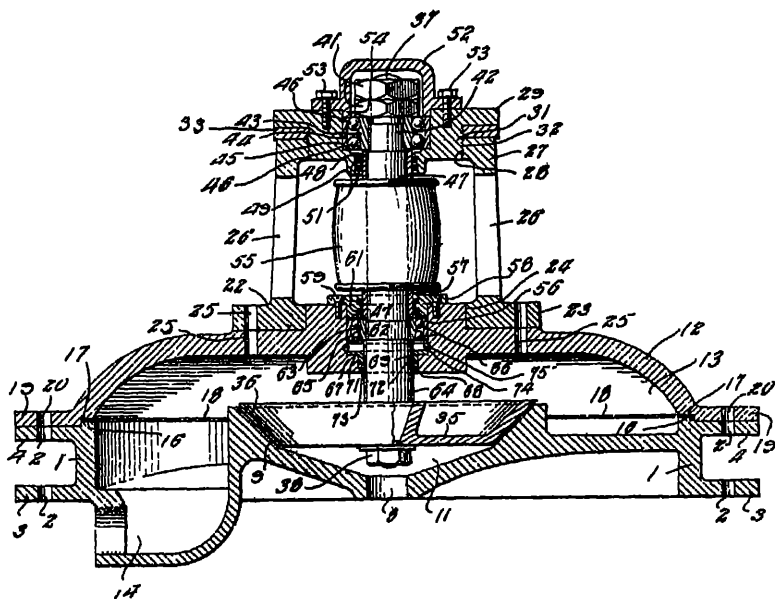
FIG. 9.—Smooth-Surface Truncated-Cone Type of Colloid Mill.

there is a considerable difference in peripheral speed between the bottom and top. The product upon coming in contact with the bottom of the rotor is carried up over the dispersion surfaces and discharged from the mill, the speed of travel increasing rapidly during the operation, resulting in a shearing action. The rotor and stator are subject to a variation in clearance through adjustment of the rotor; the clearance is calibrated by the use of a calipering device furnished with the machine. A variation in adjustment is claimed from a minimum of 0.002 inch to a maximum of approximately 0 020 inch, which covers a wide range. This type of machine has been on the market for several years and subject to actual commercial operation, and it apparently has met with some approval in cases where a smooth-surface film mill is desirable.

THE HORIZONTAL SMOOTH-SURFACE MILL

The second division of the smooth surface film type of mill includes those in which the confining film surfaces are so shaped that such film does not tend to evacuate the space by its own inertia, but in fact, actually tries to work back to the feed space. In this type of machine, the
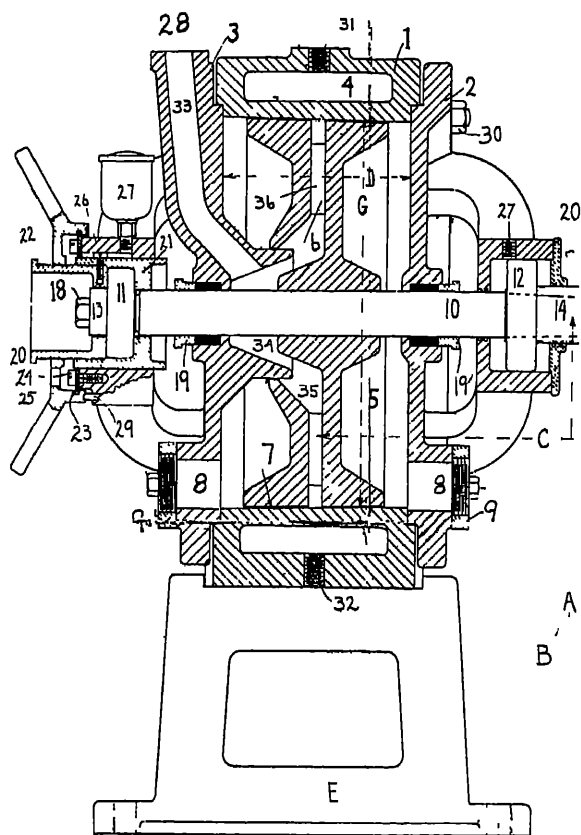
FIG. 10.—Cross-Section of Smooth-Surface Horizontal-Type Colloid Mill.

shaft is horizontal and the film gap is practically a constant quantity at any speed of rotation, differing in this respect from the mills having as working surfaces truncated discs or shallow cones. This type of machine, which is shown in cross-section as well as in perspective in Figures 10 and 11, has a short cylindrical-jacketed stator, equipped for circulation of water or steam for heating or cooling, flat end covers each carrying a gland and a ball bearing, and a rotor almost fitting the bore

of the stator and having an arrangement of radial passages at mid-length by means of which the liquids reach the film space at a pressure determined by the radial depth of liquid being whirled around between the two rotors. This depth automatically responds to the rate at which the materials are delivered to the machine. In practice, the pressure varies from a fraction of a pound to about one hundred pounds per square inch. The rotor is carried centrally between the bearings on a horizontal shaft. By feeding the product up between the centers of the rotors end-thrust is eliminated, for the thrust is approximately equal in both directions, regardless of the high film pressure prevailing on the
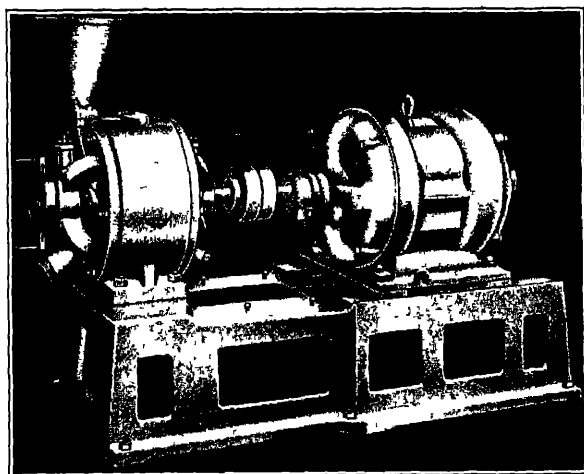
Fig 11.—Perspective of Smooth-Surface Horizontal Type of Colloid Mill.

dispersion surfaces, which may be many tons   Machines of this type are equipped with automatic calibrating devices for adjustment. The working surfaces have a very slight taper sufficient for adjustment only, and a longitudinal displacement is effected by a screw housing which opens or closes the gap.0 001 inch per half turn. The minimum clearance on such machines is 0 002 inch and cannot be passed, due to a previous adjustment to guard against this point, known as the zero adjustment. Calibration is automatically taken care of between rotor and stator by the adjustment housing while the machine is operating at full speed, thus giving somewhat of an advantage in that an operator can vary his clearance according to requirements while samples are being taken from the machine   This type of machine has enjoyed considerable popularity over the past three years in this country and has proven itself in most cases satisfactory where a smooth-surface type of film mill is desirable.

THE ROUGH-SURFACE TYPE

There are two outstanding examples of the roughened-surface types of colloid mill. These machines are designed for high speed and are quite successful in a great number of applications. Figures 12 and 13
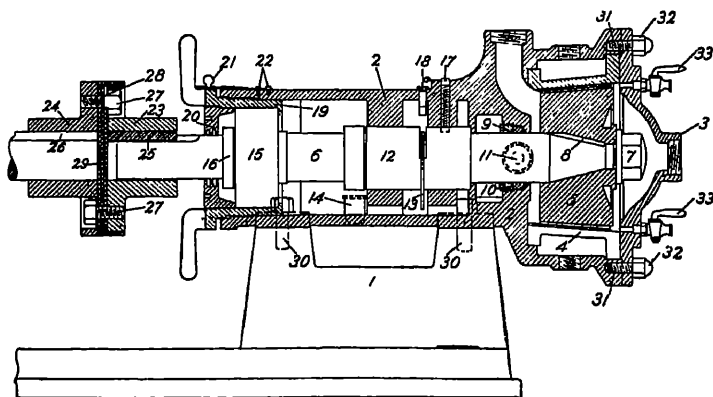
FIG. 12.—Cross-Section of a Grooved-Surface Type of Colloid Mill.

show a machine which is representative of one type of roughened sur- face The principle of this type of machine is considerably different from that of the smooth-surface mill. In this machine liquids carrying
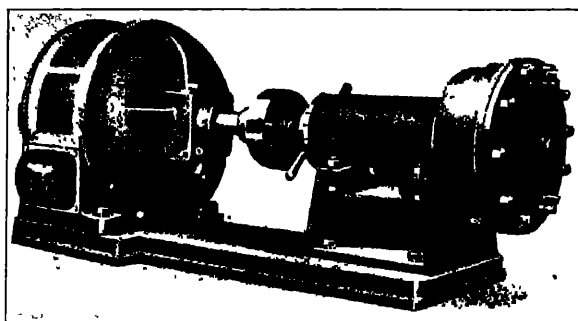
FIG 13.—Perspective of Grooved-Surface Colloid Mill

solids in suspension pass between two closely related surfaces, one being fixed and the other rotating at high speed. Both the rotor and stator have a series of grooves. The machine consists essentially of a grooved conical rotor which revolves inside of a grooved conical stator, while

the materials pass continuously through the gap between rotor and
stator. Due to the high speed at which this mill operates, there is an
intensive turbulent scissors action in combination with the hydraulic
shear which is brought about through eddy currents formed in the
grooves. Such mills operating at a speed of 3600 r.p.m. subject the
product to the continuous action above described, and the necessary
delay in dispersion period is provided for by counterpressure. It will
be noted that this machine is considerably different in principle from
the smooth-surface type of mill The rotor is carried on a shaft rotating
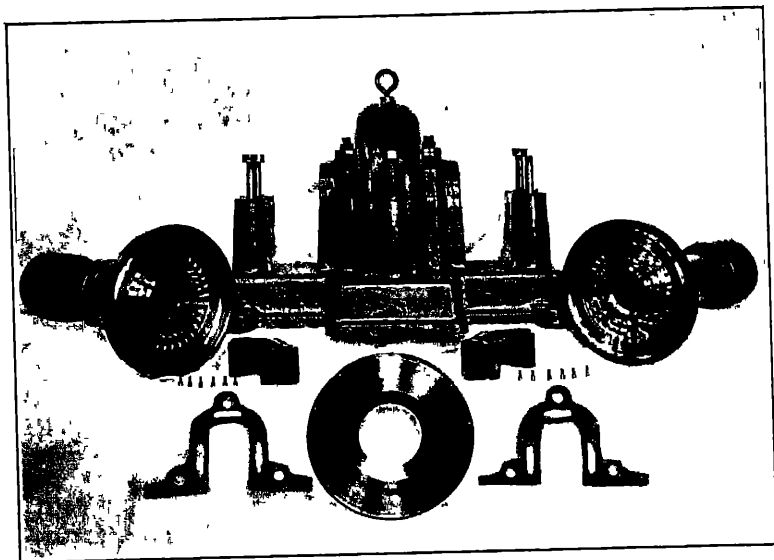
FIG 14.—Roughened-Surface Colloid Mill with Opposite-Rotating Disc.

in a horizontal position, and the materials to be emulsified or dispersed
are fed by gravity direct into the inlet of the machine, where they are
put under pressure sufficient to force the finished product into a storage
tank. This machine has been on the American market for over a year
and has proven itself satisfactory in some types of work, but like all
colloid mills, it has its definite fields of application. One of its draw-
backs has been excessive heating, hence it has not been practical for
paint work, where such heating would be objectionable. On the other
hand, this mill has proven itself superior to smooth-surface mills in
other instances, but the capacity is limited.

Figure 14 illustrates a machine using discs with lugged surfaces
rotating in opposite directions. This is a form of roughened-surface

mill which has definite fields of application and has been developed with considerable care. The machine is shown in detail. When assembled, the product is fed through the axis and discharged on the outside periphery of the flattened disc. It will be noted that the product in passing through this type of mill also receives considerable beating or hammering action. From reports, this machine seems to work quite satisfactorily on quite a variety of products. It, however, requires two motors for operation and has the disadvantage of quite a consumption of horsepower. Like other roughened-surface types of machine, it is subjected to high heating when operated at excessive speeds. Therefore, it largely depends upon the nature of the product whether this machine or others should be used There is no doubt but that the hammering or beating action on certain products is superior to the shearing action of the smooth-surface mills.

FIG. 15—Turbine Type of Colloid Mill

THE COMBINATION TYPE

Figure 15 shows a type of mill which is a combination between smooth surface and roughened surface. This machine was developed several years ago, and while numerous tests have been conducted upon it, it has not yet, to the author's knowledge, been placed upon the market The author's tests on this machine have shown it to be fairly capable of taking care of a certain type of work, and it is believed that when this machine is commercially available it will meet with a certain amount

of success   It has some of the advantages of the smooth-surface type in conjunction with the roughened-surface or beating action at high speed.   The machines manufactured to date, on the other hand, have some handicaps, one being that they cannot be adjusted for clearance but must be operated at a definite fixed clearance.   The machine is not easily cleaned, but there are a great number of commercial operations where this would not be an important factor.   Before a positive statement could be made as to the performance of this machine, it would be necessary to have more commercial units in operation than those at the present writing.   It will be noted that this machine is in principle somewhat similar to a turbine.   In fact, it is the reverse, for it is driven by outside power and the liquid containing the solid in suspension is passed through the machine, but the blades and other factors are arranged much like those in a turbine.   Attempts so far have not been made to drive this machine at excessive speeds, and it may be possible by increasing the speed that a great improvement in the results would be obtained.

COMPARISON OF TYPES

From what has been previously stated regarding colloid mills, one will appreciate that there is not a universal machine which is adaptable for all purposes.   In some instances the smooth-surface machine is in advance of the roughened-surface, while for other purposes the roughened-surface is superior, depending largely upon the problem at hand.   As a general rule, the smooth-surface machines do not heat the product as much as the roughened-surface, thus making it possible to use them more for food work.   They are easier to clean and do not have the irregular pockets for lodgment of bacteria; in other words, they are more sanitary.   On the other hand, the roughened-surface type of machine submits the product to a severe hammering action and might be looked upon as a high-speed beater.   It will accomplish certain work which a smooth-surface machine will not do.   It does not incorporate air.   Where heat is not an important factor, the roughened-surface machine will frequently prove superior.   Then again, in a large number of instances a product can be dispersed in either type of machine.   In such cases, one should decide which machine to procure according to its mechanical merits.

MAINTENANCE AND REPAIRS

The materials of construction of colloid mills are more or less standardized and consist of cast iron throughout except the shaft, and rotor and stator surfaces, which, as a rule, are of high tensile strength steel   Generally speaking, where traces of iron oxide would be detrimental to the product, or where materials being treated attack cast iron,

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Applications of Colloid Mills

The following are typical examples of some of the uses to which the colloid or dispersion mills of proper design may be put in commercial operation:

1. Emulsification of vegetable, animal and mineral oils, resins, and waxes.
2 Manufacture of water paints, calcimines, etc.
3. Incorporation of pigments in the more fluid enamels and in paints such as outside white and flat white.
4. Homogenizing of fat globules of milk for improvement in consistency and digestibility or for ice cream mix. Preparation of reconstituted milk from milk powder and sweet butter.
5. Extractions of oils, fats, resins, juices, etc, from vegetable or animal tissues as well as extraction of fibrous materials.
6. Purification of organic chemicals, liquids and solids.
7. Intimate mixing of creams, sauces and other foodstuffs where perfect blending is required.
8. Dispersion of some solids such as mica, certain oxides, fine clays, various dyes and other such materials which do not require the actual grinding operation

Many mineral colloids such as ferric hydroxide, silica gel, etc., contain water which is driven off on heating   Such material then becomes incapable of dispersion or suspension—for example, a clay heated above 100° C. Up to this temperature the natural moisture may be driven off, but there may be water of constitution, or that which is chemically combined, and after this is once driven off, the residue no longer has the properties of the original material.   Therefore, such material before excessive heating might disperse readily with the colloid mill, but such heating may make dispersion impossible   This, of course, is not always the case for there is no difficulty in dispersing a highly calcined magnesium oxide.   In fact, this is a commercial process for making milk of magnesia.   There are, however, a great number of substances to which this rule applies, especially those containing silica, iron, etc.   Very satisfactory dispersions have been made of chrome yellow, iron and zinc oxide, umber, lamp black, etc., of course, with the addition in most instances of a protective colloid.

Dispersion of Pigments

In the dispersion of pigments, the colloid mill has proven of unusual value for outside whites and flat white.   While in some instances it is claimed that the roller mill can accomplish a similar result, it is found that the capacity of the average commercial size colloid mill is far beyond that of the roller mill.   To illustrate this point, there is sold in this country a popular type of colloid mill which works on such materials with a capacity of approximately 250 to 300 gallons an hour, varying somewhat with viscosity and other changes in formula.   This means, of course, much larger output per machine unit, with a conse-

quent reduction in cost per gallon, thereby making it possible for the paint manufacturer using the machine to undersell his competitor with a similar grade of material.

SPEEDING REACTIONS BY INCREASING CONTACT SURFACE

Another interesting application of the colloid mill is for the speeding up of chemical reactions, which in a large number of cases may become almost instantaneous because of increase of dispersion and surface area of the dispersoid To illustrate such operation, one might remove the impurities from certain oils by emulsification followed by the breaking of such emulsion, when the impurities would remain in the water phase with the emulsifying agent. An example of such purification is that of the production of carbolic and cresylic acids from tar oils. In this instance the carbolates separate upon the breaking of the emulsion. Other possible uses where contact is important is that of continuous saponification where the colloid mill might, in some instances, be of considerable value due to instant contact over large surface area. From this one would infer that a future possible use of the colloid mill would be in the case of contact catalysis in heterogeneous systems. This may be brought about by the conversion of one or more of the reacting substances into active form

It is believed that in contact catalysis the mechanism may be explained in time by the theory of oriented adsorption resulting in activation of the various groups which make up the molecules.[5a] The essential point is that it would have a tendency to cause activation and breaking of the regular or residual valence causing the active masses or free radicals to combine. If the function of the catalytic agent is to produce these free radicals, there is a possibility that the colloid mill may be of great assistance, especially in the case of a solid catalytic agent. It is common knowledge that such agents become inactive very easily, or as commonly stated, the catalyst becomes poisoned, and one of the difficulties seems to be to keep the catalyst active. As reaction is assumed to take place at the surface of the catalytic agent, it may be that by increasing the surface area the surface actions might be speeded up before it is prevented from such contact or before the reaction velocity is decreased to any great extent. Any piling up of the reacting product on the surface of the catalyst will decrease the reaction velocity, and thus hinder or prevent the reacting substances from coming in contact with the catalytic agent.[15-5] Therefore, with small quantities of a solid catalytic agent equally dispersed throughout the mass, this poison effect of such agent may be reduced somewhat, due to intimate contact throughout the mass at the same instant. While the use of a colloid mill

[5a] Langmuir, *J. Am. Chem. Soc.*, **38**, 2270 (1916).

may not in some instances be of any value in such reactions, the above is merely offered as a suggestion to those who are working in such field. It would largely depend upon the nature of the problem whether a colloid mill would be of value in such work The colloid mill does not accelerate all chemical reactions, but it would at least be worth investigating for the purpose of improving of contact catalysis.

De-inking Paper

The recovery of pulp from old newspapers and various publications such as magazine stock has been accomplished by use of the colloid mill. In this process the paper may be de-inked and dispersed in one operation, and with the addition of a small quantity of solvent to the water medium, lithographing inks may be removed as well. The quantity of the solvent can be as low as one or two per cent. Such paper has been recovered from the de-inking process without apparently shortening the length of the paper fiber or impairing its strength. Such work, however, must be performed on the proper type of mill so as to accomplish a rolling action on the fibers which are sufficiently flexible so that they are not destroyed They can be washed upon a screen and recovered apparently in their original condition. The disadvantage of the relatively small capacities of colloid mills makes it rather difficult to compete with the beater.

Solvent Extraction

Apparently one of the important uses for colloid mills is for extracting materials such as tannin, ginger, vanilla bean, cascara and belladonna, as well as other barks and herbs. This extraction process can be applied to a great number of vegetable tissues for the extraction of essential oils or other ingredients which are soluble in the various solvents. The success of the colloid mill in this field is due to its shearing action, giving fine dispersions of the fibrous materials, while not actually destroying the fiber, putting it in such shape that it has intimate contact with the solvent, in some instances as individual fibers, this, of course, increasing the extent of extraction as well as the time required. It is merely a problem of intimate contact of the solvent with great surface area within a short instant of time. Not only does it give rapid extraction in a great number of instances, but as a rule products which have previously been extracted by percolation may show an additional recovery by subjecting the product to dispersion in the presence of the solvent Such extractions, of course, in a great number of instances, would not only accomplish this in a better form, but eliminate percolating towers and other equipment occupying large spaces, doing away with a great amount of loss of solvent through

evaporation. The entire product from the colloid mill could be discharged into a closed tank equipped with condensers, if necessary to recover the solvent lost through evaporation. The problem, of course, is to clarify this material, which can be done in a great number of instances by the use of a proper type of clarifier, based upon the principle of the centrifuge. By use of such equipment it is possible to make rapid extractions within a relatively small space and, in a great number of instances, have a far better yield of recovery from such extractions It has been surprising to find the high yield which can be obtained by this means.

INKS AND CARBON PAPERS

The uses of the colloid mill are greatly extended in some industries where it can be used in conjunction with other equipment. To illustrate such an instance, we shall consider the case of carbon inks for use on carbon paper. It has been found that with some types of colloid mills such carbon inks can be made direct, of sufficient particle size, for use in sales note books or where carbon paper may consist of coarser particle size. For the finer typewriter carbon papers it has been found of value to use the mill in conjunction with grinding equipment. In such operations the pigment or coloring material in conjunction with the molten waxes, stabilizers, etc., is passed through the colloid mill at a fair capacity, giving a dispersion sufficient for rough carbon papers. The dispersion is then sent through one of the regular commercial type of wet-grinding machines, for instance, a stone mill, and in this way a perfect product for use in the finest grade of carbon papers is obtained. It is found that the colloid mill gives a fairly fine dispersion but there are a few occasional odd particles of carbon not completely dispersed which appear when the material is spread upon glass for testing. After treatment through the colloid mill the product might be 98 per cent dispersed. By using a colloid mill in conjunction with other grinding equipment the work can be completed to meet commercial requirements and a great deal of time saved.

In the above instance much depends upon the type of pigment or carbon used. There is a great variety of carbons. Of course, no great difficulty would be encountered in dispersing lampblack directly through the colloid mill without following this with a wet-grinding process, for in this instance the carbon particles are merely grouped together and only require dispersion. On the other hand, some types of carbon are firmly bound and the carbonaceous material may be of a hard and gritty nature. It is in such instances that the grinding equipment should be used in conjunction with the colloid mill. It is a well-known fact that Prussian blue is very difficult to disperse and

it has been found in practice that where Prussian blue is used for carbon inks, the colloid mill can be assisted greatly by the use of a wet grinding process in some instances before passing through the mill, and on other occasions after passing through the colloid mill, depending upon the nature of the work.

LACQUERS

In the manufacture of a lacquer finish, such as is popular for automobiles, furniture, etc., the so-called colloid mill cannot be expected to produce a product at a rate of treatment of 300 to 500 gallons per hour which will compare favorably with a product made by 60 to 80 hours of continuous wet grinding. The colloid mill may, however, be used for dispersion of the pigment in the presence of the lacquer solvent and a dispersion obtained of a very fine particle size. In such dispersions, of course, no nitrocellulose should be present. When this product is discharged from the mill, an occasional large particle will show when spread in a film on a smooth surface, and we might say, for argument's sake, that it is 98 per cent dispersed. It is possible to produce an ideal product from this dispersed material by then incorporating the nitrocellulose and after complete blending passing the lacquer through a clarifier operating at high speed, thereby removing the coarser particles In such work the speed of the clarifier, of course, must be carefully regulated, so as to throw out only the larger particles of pigment and not remove the fine dispersed material. The percentage of coarse material, or that which would not pass the requirements for a high-grade lacquer, is relatively small after treating through a colloid mill, hence, the bowl of the clarifier will not become caked with the material thrown out for some time. This makes almost a continuous process for the production of an ideal lacquer and eliminates long hours of grinding in batches, with, of course, considerable saving and increased production. This method of manufacture of lacquers has passed through the laboratory stage and the results are very promising for commercial application on a large scale in the very near future.

The method of treatment of the pigment in conjunction with the lacquer solvent and then the blending with the nitrocellulose has interesting applications, where it is not necessary to use the clarifier The colloid mill under proper conditions gives sufficient dispersion of the pigment for coating on leather and other surfaces where the particle sizes of the pigment are sufficiently small to penetrate the pores of the leather The author has seen lacquer coatings of such material made which worked very satisfactorily on thin leather, with very high covering power. The leather could be rolled up without

cracking the film. In instances where the product was not used on a hard surface, the dispersion in the colloid mill was sufficient, and of course, gave the manufacturer large production at a relatively low cost, with a greatly simplified process.

LITHOPONE IN PAINT

The application of the colloid mill in the paint industry has met with a great deal of success in certain fields, as previously stated (see p. 164). The colloid mill can also be used to great advantage in the dispersion of lithopone, which, of course, is merely deflocculation of the precipitate formed in the manufacture of this product. From the work accomplished in this field so far, one of the important factors has been that of heating, and it has been found that certain types of colloid mills can be used very successfully without overheating the product. It is found that certain types which apparently perform the dispersion are not practical for this kind of work due to the excess heating, except in water dispersions.

FUEL OILS

Attempts have been made from time to time to use various types of colloid mills for the dispersion of coke in fuel oil after the cracking process, and such work has met with a relatively marked degree of success in small-scale operation The problem in such instances, of course, is to get a sufficiently finely divided state of the coke residue after the cracking process so that it will not settle out or clog the spray nozzles when the oil is used under the boiler. One of the main difficulties encountered in the past seems to have been to get machines of sufficient capacity to handle the fuel oil in tank-car lots within a relatively short period of time. The average colloid mill now on the market usually has a maximum output of from 500 to 700 gallons per hour, depending largely upon the viscosity of the product, and while attempts have been made to build oversize colloid mills with many times this capacity, mechanical difficulties have been encountered. On such work a colloid mill would have to perform on almost continuous operation throughout the year. This of course is a difficult problem for a colloid mill, due to the fact that these mills operate at high speed The average colloid mill operates at 3600 r.p.m. and is usually directly connected by a flexible coupling to an electric motor. In other instances such machines operate at an even higher rate of speed, connected with a steam turbine. There are, therefore, mechanical difficulties to operating 365 days a year continuously. Where colloid mills are operating six to eight hours a day, with the improvements recently made there should not be a great deal of

trouble encountered   While there would not be any great wear or tear when operating a few hours a day, it is quite different from operating continuously day and night over long periods without shut-down

SPRAY DRYING

The colloid mill has very important applications in connection with spray drying or the drying of products in a finely divided state by dispersion in air, technically spoken of as aerosols.   By proper dispersion of solid material in the presence of a liquid medium through the colloid mill, taking advantage of the hydraulic shearing action, such product, of course, can be reduced to a very small particle size at a rapid rate by a continuous process.   This dispersed product can then be passed directly into the spray dryer in such finely divided state, if carried out under proper supervision.   This opens up new applications where it is desirable to have the product in a dry state. The author has observed such products in a dry state where the particle size was sufficiently small so that the dry material poured like a liquid.   It is practical to produce such products commercially, but the work must be conducted under strict technical supervision by one well versed in the various basic principles of colloidal dispersion. Under such circumstances it can be carried out from day to day with comparatively few difficulties.

PLATING OF EMULSIONS

There are numerous instances where the colloid mill may be used to great value in the making of emulsions.   The usual emulsions for medicinal uses are well understood and appreciated by most readers It is not so well known, however, that the colloid mill may be used for making an emulsion as an intermediate product in accomplishing the finishing of some other product   To illustrate this point more clearly, we might take a specific example: for instance, if a proper oil-in-water type of emulsion is made by the use of the colloid mill, it is well-known that the oil globules carry negative charges, hence will migrate to the positive pole or anode   Therefore, by passing an electrical current through such an emulsion, the oil globules may be deposited upon the anode or positive pole   A very interesting application is that mentioned in Chapter XII, of making an emulsion of blown oils or asphalt, then plating them out onto metal that it is desired to give a japan finish.[6]   After plating out on this surface it, of course, must be baked.   A similar process is now used in the manufacture of anode rubber from latex

[6] Davey, "Making and Breaking of Emulsions," Colloid Symposium Monograph, Vol. 4, Chemical Catalog Co., New York, 1926, p. 38.

RUBBER COMPOUNDING

Other interesting applications are the fine dispersion of pigments or colors used for rubber fillers or for rubber compounding. The colloid mill is now used to great advantage for making all types of industrial emulsions, but its application for making emulsions as a sort of intermediate for accomplishing other purposes is relatively new, and promises important developments when conducted under proper guidance.

VAT DYES

A very interesting application of colloid mills is for the dispersion of vat dyes, on which a great amount of work has been done over the past few years in taking this process from the laboratory into commercial production   By use of the colloid mill it has been possible to make vat dye pastes by direct dispersion of the dye in the water phase, eliminating all coarse or gritty material so that the dye would not settle or scratch the rollers when used for printing on cloth.   It also does away with the little particles which might cause blots or blemishes when printing in the textile trade, and it is possible to make a smooth paste which apparently is very much desired for such work In connection with this work, it might be well to point out that quite a study of stabilizing agents is most essential.   When the vat dye is properly dispersed in the water, it will not flocculate but will remain in sufficiently fine dispersed condition so as not to settle out of the water phase.

GENERAL CONCLUSIONS

It requires quite an extensive study in this field to become familiar with such work sufficiently to carry processes into commercial production.   While a great number of dispersions have been worked out and put into commercial application, it has been found that there are no general emulsifying agents that cover all cases   It depends a great deal upon the nature of the dye, for example, as to which type of agents are necessary   Also in solving such problems it has been very difficult to obtain a type of dispersing agents which will not affect the covering power of the dye, for in some instances where ideal dispersion is accomplished, it is found that the covering power has somewhat diminished.   The colloid mill works very successfully in this field, but it should be understood that the mere purchase of the mill is not all that is required.

Chapter XV.

Laboratory Methods and Physical Testing of Properties.

As has been previously pointed out, the matter of viscosity in colloidal dispersions is of great importance. We know that as we increase the surface in fine dispersion there is a relative increase of viscosity, and that the viscosities vary greatly in various dispersions and emulsions. We have not been able to use viscosity as a guide in most work on colloidal dispersion, there are, however, some instances in which viscosity determinations are of value.

Viscosity is measured by means of the instrument known as the viscosimeter The instrument is ordinarily used for making comparisons only. Numerous forms of viscosimeter are now on the market. We may classify these into three important types:

1. *The capillary tube viscosimeter,* dependent upon the flow of a measured quantity of liquid through a capillary tube. A simple form of this apparatus consists of a U-tube with a bulb attached to each end, or a type of tube in which there is a small capillary opening. For testing, a measured quantity of liquid must flow through the capillary opening to a definite mark on the other side of the capillary tube, at a definite temperature. The time of flow through the tube is noted.

2. *The torsional viscosimeter,* in which a measurement is made of the resistance of the liquid to torsional strain. This viscosimeter usually consists of a metal disc suspended, by means of a wire, in the liquid being examined, contained in a metal cup which is usually jacketed for maintaining temperature. The wire suspending the metal disc passes through a plunger fixed at the bottom of the cup, while the other end of the wire is held between grooved pins provided with a graduated dial The cup containing the liquid on which the viscosity is being determined is rotated at high speed and the friction between the liquid in the cup and the metal disc causes a torsional strain on the wire, which in a short interval of time becomes constant. The

dial which can be graduated in degrees is then read and from the angle of torsion the viscosity may be calculated.

3. The third type of viscosimeter is known as the *falling sphere viscosimeter,* and is based on the principle of determining the time required for a sphere of definite weight and size to fall through a measured column of the liquid at a definite temperature. This type of viscosimeter consists of a tube with a fairly large internal diameter —approximately 2 cm. The cylinder is usually jacketed so as to maintain constant temperature, and is marked into definite divisions, according to a scale. The tube is filled with the liquid to the level of the top mark. A small steel ball is dropped into the liquid and the time required for the ball to fall through each 5 centimeters of the column is taken. After the time has been observed through three or more of such divisions, it is averaged. From this the absolute viscosity may be calculated by the use of Stoke's law for settling spheres. Specific viscosity, of course, can be determined by comparing this liquid with water, if such is required.

The above briefly describes the typical varieties of viscosimeters used in making determinations. All laboratories conducting research or development work pertaining to colloidal dispersions or emulsification should find one of these instruments valuable.

TYPE OF EMULSION

It is often difficult to determine which type of emulsion, the oil-in-water or the water-in-oil, has been obtained when it is first produced. There is a very simple method of determination, however. Water added to an emulsion of the oil-in-water type will dilute it readily, because the water is in the outer phase, and oil added to a water-in-oil type of emulsion will readily mix with the oil phase. In short, an emulsion will mix with more of the constituent which forms the external phase but not with that which forms the internal phase.

Another method which is sometimes used employs an oil-soluble dye, such as Sudan 3 or Scarlet R. These dyes give a spreading color in an emulsion of the water-in-oil type, because they dilute with the oil phase. If such emulsion were of the oil-in-water type, the dye, not being soluble in the water phase, would not spread or color the mixture The oil-in-water type of emulsion will also conduct electricity and heat more readily, while the water-in-oil type is a non-conductor of electricity. It is not necessary, as a rule, however, to make such tests to determine the type of emulsion. The common practice is merely to attempt to dilute with water.

OIL ABSORPTION

It is quite obvious that the degree of absorption of finely ground pigments, clays, etc , varies greatly. In order to estimate in a qualitative way just how much oil such materials will absorb, a very convenient method was devised by Coleman [1] This test, briefly, is a measure of the amount of absorption of oil or water by a definite weight of the solid pulverized material. It is used quite extensively by paint manufacturers for determining the absorption of oil in the making of putty, and for obtaining absorption of various fine clays, fillers, etc. The test is conducted as follows: Ten grams of the dried pulverized material, which should be free from all surface moisture, is placed in a small porcelain dish. A 25-cc. burette is filled with linseed oil or distilled water, and the oil or water carefully dropped into the dried material. By means of a spatula the material is worked until the consistency is that of a putty. The reading on the burette is then taken and multiplied by ten to give the equivalent in cc absorbed per hundred grams This test is not exact, of course, the personal equation enters into it as to just the proper consistency at which to stop adding the liquid, but the same operator can check various samples quite closely. This test is very valuable for comparative purposes with different grades of fine dry materials, having been found useful in classifying and grading various Portland cements, fine clays, ground pigments. etc. From this test, important information can be obtained in a qualitative way on particle size of dry materials

PARTICLE SIZE

Before discussing the usual methods of determining particle size, it is well to mention the classification of dimensions so one may be able to obtain an idea of the various sizes in colloidal dispersions, to which reference has been made frequently in this book under various discussions.

The ordinary unit of measurement for colloidal particles is the micron, frequently designated by μ This dimension is 0 001 mm. or 0.0001 cm., which is equivalent to 10^{-4} cm. This covers the usual measurements for larger particles. The smaller unit is known as the millimicron, or submicron, designated by $m\mu$ or $\mu\mu$, from which it is obvious that it is one one-thousandth of a micron, or 0 0000001 cm   The true colloidal zone is usually assumed to start at 0 2 μ, or 200 $\mu\mu$, as the upper limit of the particle size, and from there continue down to the molecular. In this zone, of course, we have transparency, for such particles are smaller than the light wave, which for yellow light is

[1] Coleman, *U. S. Bureau of Soils Bull ,* 52 (1908)

about 600 $\mu\mu$ or 0.6 μ. Colloidal properties, however, begin to appear long before particles approach this size, and we find that ordinary dispersions in which the particles are one micron, or even larger, in size, exhibit certain colloidal properties, such as increase in viscosity, taking on the particle charge and the other characteristics mentioned throughout this book in the various chapters. Investigations of particles of this size must be carried on entirely from the colloidal viewpoint. In emulsions the globules may be of very large size, but the colloidal phenomena become more pronounced as the particles approach smaller sizes.

The various particle sizes can be determined in a qualitative way by the various methods of filtration. As an illustration, ordinary filter paper will not permit particles to pass that are over 5μ in diameter, while a hardened filter paper will hold particles over 2μ in size. Clay filters may retain particles 0.1μ in diameter. It is obvious that the pores of the filter must be finer than the diameter of the dispersed phase in order to separate the solid particle. In order to separate, by methods of filtration, colloidal dispersions which are below the above particle sizes, it is necessary to resort to the ultrafilter in which use is made of what we might call jelly filters. In making such filters, silicic acid gels and gelatin are frequently used, as well as nitrocellulose solutions in various solvents Bechhold,[2] in making ultrafilters, used flat layers of filter paper impregnated with such jellies. By building up in laminated strips it is possible to make such filters withstand pressures of 20 atmospheres or more, and to vary the size of the pores considerably. The size of the pores of such ultrafilters varies with the material used but it is possible to go to sizes far below those of colloidal solutions of the common types Of course all bacteria may be readily removed by the use of ultrafilters.

The determination of particle size is based on counting the number of particles in a definite volume of known concentration, which is a tedious operation, or by the use of what is known as Stokes' law for sedimentation. This law was worked out and used by Sir C. G. Stokes a great number of years ago and is based on movement of spheres [3] While it does not apply to particles of various shapes, it is found to be of considerable value for comparative purposes, regardless of this fact In emulsions, however, where the globules are spherical in shape, as a rule, Stokes' law applies with a fair degree of accuracy The closer the particles approach the spherical shape, the more accurate the determination becomes. Stokes' law is based upon the resistance F of a liquid of viscosity n and density p, towards the movement of a sphere

[2] Bechhold, *Z phys. Chem.*, 64, 328-343 (1908)
[3] Stokes, *Phil. Mag*, 29, 60, 62 (1846).

of radius r, density p, and velocity v, the moving force being gravity (G), measured in dynes. The equations are as follows:

$$G = \frac{4}{3} \pi r^2 (\rho - \rho_1) g \qquad \text{I}$$

$$F = 6 \pi n r v \qquad \text{II}$$

$$\therefore V = \frac{2}{9} \frac{r^2 (\rho - \rho_1) g}{n} \qquad \text{III}$$

The radius of the particles may be determined from their rate of fall by means of the third equation, and size can be determined provided the particles are spherical in shape

Stokes' law of sedimentation applies not only to spheres in liquid media but also to aerosols or liquid drops dispersed in gaseous media. Millikan [4] investigated this field quite extensively and conducted some very interesting experiments with oil droplets in which the oil was sprayed in the form of a fine mist in a chamber above an electrode Individual particles penetrated through a small pinhole in the upper electrode, and by applying a force of several thousand volts between two electrodes, the force of gravity upon the oil droplets was offset. The particle could remain in suspension between the two electrodes by having the opposite charge on the upper electrode After such globules were permitted to fall through a definite space, they could be brought back to their original position by applying the proper voltage to offset the pull of gravity, thus making it possible to observe accurately the rate of fall. By changing the pressure of the gas, different values could be calculated, and it was found that such spheres closely conformed with Stokes' law of sedimentation and the size of the particles could be calculated with extreme accuracy

It was found that when oil was sprayed into a gas medium in the form of mist, such particles always took on an electrical charge, or a difference in potential was created Photographs made by Wells and Gerke [5] indicated that such particles took irregular paths and that Brownian movement was quite effective in such influence. The amplitude of such oscillation results in accurate measurement of the distance traveled by particles in a definite interval of time under the influence of known electrical force By such methods of measurement the range and distribution of the sizes of particles forming an aerosol can be measured. Individual particles may be weighed by applying definite electrical forces against the pull of gravity and velocities can be obtained in excess of those of gravity or Brownian movement.

[4] Millikan, "The Electron," University of Chicago Press, Chicago, **1924**, p. 118.
[5] Wells and Gerke, *J. Am. Chem Soc.*, 41, 312, 329 (1919)

Stability

Suspensions, even beyond the colloidal sizes, can in time be separated by sedimentation, but this is very difficult to accomplish simply under the influence of gravity As the mass becomes larger, it, of course settles more readily; on the other hand, if it is sufficiently small, the particle must remain in permanent suspension. Sedimentation takes place only when these particles increase in size. This property of dispersed particles is a function of their mass. In order to facilitate the settling of fine particles, one resorts to centrifugal force, and the usual procedure is to use the centrifuge. "The most powerful centrifuge will cause only slightly more coalescence of emulsions than may be secured after long gravity settling."[6] It would seem that coalescence is brought about as readily by mere contact between the globules, and that the pressure of one globule against another, brought about by high centrifugal force, will not greatly assist in bringing it about. Regardless of this fact, the laboratory centrifuge is of great assistance in determining the stability of an emulsion by determining how long such emulsion will stand centrifugal treatment without creaming or separating out water. While it is true the same result could be brought about by gravity through regular settling methods, this takes time, whereas by use of a small laboratory centrifuge such determinations can be made with a fair degree of accuracy within thirty minutes. By noting the time under such centrifugal treatment, at definite temperature, and comparing this with similar separations by the action of gravity, allowing the product to stand in closed containers over a period of time, a factor may be established for the product After this has once been determined, the stability of such product when it is made up can be fairly accurately estimated by use of the centrifugal principle.

The speed of the centrifuge will depend upon the particle size, in order not to precipitate the dispersion;[7] for instance, at 40,000 r.p m. fine particles of colloidal gold will be precipitated, while other finer materials may withstand such treatment. On the other hand, if this same material were treated by a super-centrifuge with a speed of 40,000 r.p m., and with proper peripheral speed to increase the force of gravity 42,000 times, practically all of the particles would be precipitated. Very few colloidal dispersions could withstand this treatment without throwing out all of the solid matter therein. It is entirely a matter of particle size. The smaller such particles become in mechanical treatment, the more stable, hence the greater the amount of centrifugal

[6] Ayres, in Alexander's "Colloid Chemistry," Chemical Catalog Co., New York, 1926, p. 855.
[7] Clark, Colloid Symposium Monograph, Vol. 2, Chemical Catalog Co., New York, 1925, p. 174

force which can be applied without throwing such particles out of suspension.

<p style="text-align:center">OPTICAL OBSERVATIONS</p>

If the mass of a colloidal substance in dispersion is represented by M, the number of colloidal particles by N, and the density of such colloidal substance by D, the volume of single particles, V, can be calculated according to the following formula:

$$V = \frac{M}{DN}$$

In this formula, the mass M of substance per given volume of the dispersion can be obtained directly, if the concentration is known. In order to obtain N, the number of particles in a definite volume, they must be counted by some means, of which the microscopic is probably the most popular. The density D of the substance from which the dispersion is made can be determined by various methods. Therefore, all the quantities in the above equation can be ascertained with the exception of V, which, of course, is calculated on the assumption that the particle is a sphere. It is quite obvious that errors are involved, for there are few solid particles in dispersion which are perfect spheres.

In cases where the particles are too small to be seen by the microscope, it is necessary to use the ultramicroscope. This instrument has been found to be of great assistance to the colloidal chemist when working with very small particle sizes, below the limit of the ordinary microscope. In order to differentiate between suspensions and solutions, it is well to review the scale used for particle sizes, which has been previously given (page 174). In suspensions, the particles may vary greatly in size, but apparently the lowest particle size which has ever been measured, even by the use of the most finely equipped ultramicroscope, is 1 $\mu\mu$. Dispersions in which the particle size is smaller than 2 $\mu\mu$ appear clear when viewed in ordinary daylight with the unaided eye. Particles smaller than 1mμ, or below the limits of the ultramicroscope, are frequently referred to as ultramicrons and are closely approaching the true homogeneous solution or molecular sizes. Particles larger than 100 $\mu\mu$ will settle out on long standing when in a low viscosity liquid, and can be removed by filters, while particles which range in size from 100 $\mu\mu$ and 10 $\mu\mu$ will not settle out, even in low viscosity liquids, nor will they be removed by ordinary filtration methods. Brownian movement begins to be noticeable at about 2 microns or 2000 $\mu\mu$, and while it can be observed in larger particles, it becomes more active as the size decreases, so at 1 micron it is fairly active.

A general classification of particle size, as outlined by Siedentopf,

is as follows: Particles which are too small for ordinary microscopic vision are classified as ultramicroscopic, this applies to particles whose diameter is less than 250 $\mu\mu$. If the ultramicroscopic particle can be rendered visible, it is termed sub-microscopic. If the ultramicroscopic particle cannot be rendered visible, it is termed amicroscopic, and such particles are known as amicrons.

THE ULTRAMICROSCOPE

The discovery of the ultramicroscope by Zsigmondy and Siedentopf [8] has been of great assistance in observing particles beyond the limit of the ordinary microscope. The operation of the ultramicroscope is based entirely upon the visibility of objects by reflected light. This is usually illustrated by small particles in suspension in the air; for instance, when beams of light pass through air containing small dust particles, they are reflected. Such light strikes the particles at a proper angle to reveal objects of small dimensions which are not ordinarily visible. This idea applied to the microscope, is the principle of the ultramicroscope In observations with the regular microscope by use of transmitted light, very small particles, such as colloids in dispersion or particles less in size than the wave length of the light, of course are not observed. By use of reflection when the proper angle is used to obtain such reflection, it is possible to see particles less in size than half the wave length of the light employed for illumination. Such particles appear as small points of light, regardless of their shape or form, and each appears many times larger than it actually is. The particles are not defined in their true shape by such observations but are merely rendered visible because of diffraction. The observations in the ultramicroscope are frequently compared with the stars as observed in the sky at night; in fact, the condition is very similar.

If a beam of light were passed through dust-free air and an attempt made to observe such beam at right angles, nothing would be seen. Also, when a beam of light is passed through a true solution, such a beam cannot be observed at right angles If the air or liquid contains suspended particles, however, these disperse the light. The path of the beam can be readily traced. This is known as the Tyndall effect. Tyndall [9] demonstrated that if a parallel beam of light is transmitted through homogeneous fluids, the path of the ray appears dark, whereas if solid particles are present, the path of the ray is illuminated. Where we obtain a faint beam of light, but no particles are observed, it is an

[8] Zsigmondy and Siedentopf, *Ann. Phys.*, **10**, 1 (1903), *also see* Cotton and Mouton, *Compt rend*, **136**, 1657 (1903).
[9] Tyndall, *Phil. Trans.*, **160**, 337 (1870); *also see* Mecklinburg, *Kolloid-Z*, **14**, 172-181 (1914).

indication that a dispersion exists but such particles are extremely small.
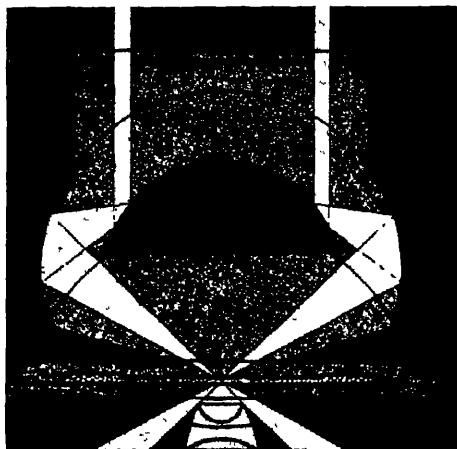
Fig. 16.—Type of Condenser for Ultramicroscopic Use.

Zsigmondy and Siedentopf, having observed that the particles which are sub-microscopic could be rendered visible by side illumination, per-fected apparatus for such observations, based on the principles that the particles must be illu-minated as intensely as possible, and that only the reflected light from the particles must be observed by the eye. hence, the field in the microscope must be kept dark and light per-mitted to enter only from the sides.
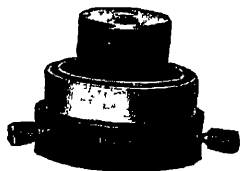
Fig. 17. — Dark-Field Condenser for Ultra-microscopic Work
Courtesy of Eimer & Amend

Several types of ultramicroscope are now on the market, the most elementary being somewhat similar to two microscopes, at angles of 90 de-grees to each other. Through one a beam of light is passed into a cell containing the liquid, the cell being in entire darkness except for the beam. The eye of the observer is at an angle of 90 degrees from the beam, observation being made through the other microscope.

Modifications of this first type have been made, and such observa-tions are now frequently made by use of what is known as dark-field illumination. This consists of the ordinary microscope with a center stop in the condenser, so as to allow the light rays to pass through only at a definite angle, and making it impossible to observe the object by transmitted light. Besides the usual dark-field illuminator there

are other forms, among which is the cardioid condenser. In this, very oblique rays of light pass through the liquid but do not enter the objective of the microscope, the field thereby appearing dark. Any solid particles in the path of these rays, however, reflect light and appear brilliantly illuminated. Such particles, due to their small size, of course, are in active Brownian movement. By use of such instruments it is easy to differentiate between a solution and a colloidal dispersion, where the solution does not contain any foreign substance in suspension, and the so-called colloidal solution is within the limits of the instrument.

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